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Water Quality Assessment: A Screening Procedure for Toxic and Conventional Pollutants, Part 1

Tetra Tech, Inc.
Lafayette, CA

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New technical developments in the field of water quality assessment and a reordering of water quality priorities prompted a revision of Water Quality Assessment: A Screening Methodology for Nondesignated 208 Areas (EPA-600/9-77-023). The utility of the revised manual is enhanced by the inclusion of information on the accumulation, transport, and fate of toxic chemicals in the environment. The new subtitle--A Screening Procedure for Toxic and Conventional Pollutants--reflects the added data.

Applying the manual's simple techniques, the user is now capable of assessing the loading and fate of conventional pollutants (temperature, biochemical oxygen demand-dissolved oxygen, nutrients, and sediments) and toxic pollutants (from the U.S. EPA list of priority pollutants) in streams, impoundments and estuaries. The techniques are readily programmed on hand-held calculators. Most of the data required for using these procedures are contained in the manual.

Because of its size, the manual has been divided into three parts. Part 1 contains the introduction and chapters on the aquatic fate of toxic organic substances, waste load calculations, and the assessment of water quality parameters in rivers and streams. Part 2 continues with chapters on the assessment of impoundments and estuaries and appendices A,B,C,E,F,G, and H.

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A Screening Procedure for Toxic and Conventional Pollutants

Part 1

by

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FOREWORD

As environmental controls become more costly to implement and the penalties of judgment errors become more severe, environmental quality management requires more efficient analytical tools based on greater knowledge of the environmental phenomena to be managed. As part of this Laboratory's research on the occurrence, movement, transformation, impact, and control of environmental contaminants, the Technology Development and Application Branch develops management or engineering tools to help pollution control officials achieve water quality goals through watershed management.

Basin planning requires a set of analysis procedures that can provide an assessment of the current state of the environment as a means of predicting the effectiveness of alternate pollution control strategies. This manual contains a description of a set of consistent analysis procedures that can help to accomplish these tasks. It is directed toward local and state government planners who must interpret technical information from many sources and recommend the most prudent course of action that will maximize the environmental benefits to the community and minimize the cost of implementation.

The manual was prepared in cooperation with the Office of Water and the Center for Environmental Research Information. The Office of Water is reviewing the manual for its potential use as a screening guide for the Wasteload Allocation-Total Maximum Daily Load program. User comments on the methodologies in the manual are encouraged and should be directed to the Center for Water Quality Modeling at the Athens Environmental Research Laboratory.

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Director
Environmental Research Laboratory
Athens, Georgia

ABSTRACT

New technical developments in the field of water quality assessment and a reordering of water quality priorities prompted a revision of Water Quality Assessment: A Screening Methodology for Nondesignated 208 Areas (EPA-600/9-77-023). The utility of the revised manual is enhanced by the inclusion of information on the accumulation, transport, and fate of toxic chemicals in the environment. The new subtitle--A Screening Procedure for Toxic and Conventional Pollutants--reflects the added information.

Applying the manual's simple techniques, the user is now capable of assessing the loading and fate of conventional pollutants (temperature, biochemical oxygen demand-dissolved oxygen, nutrients, and sediments) and toxic pollutants (from the U.S. EPA list of priority pollutants) in streams, impoundments, and estuaries. The techniques are readily programmed on hand-held calculators. Most of the data required for using these procedures are contained in the manual.

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CHAPTER 1

INTRODUCTION

1.1 BACKGROUND

In 1977, the United States Environmental Protection Agency published Water Quality Assessment: A Screening Method for Nondesignated 208 Areas (Zison *et al*., 1977). This document was intended as a simplified methodology that water quality planners in nondesignated 208 areas could use to perform preliminary assessments of surface water quality. The method covered primarily the identification of problem areas for sediment, nutrients, dissolved oxygen, and some urban pollutants in streams, lakes and estuaries.

The original methodology was used by its developers, Tetra Tech, Inc., as instructive materials in EPA workshops on water quality assessment. It was also used in an EPA project designed to test the methodology. In that project, elements of the procedures were applied to the Sandusky River in northern Ohio and to the Ware, Patuxent, Occoquan, and Chester Rivers in Virginia and Maryland. Testing results were favorable for phosphorus and reasonable for nitrogen (nitrate loading was a problem) and were reported in two publications (Dean *et al*., in press; Dean *et al*., 1981).

As feedback was acquired from individual users and workship participants, there arose a need to reassess the methods available in light of new technical developments and new priorities in water pollution assessment and control. To this end, the original screening method (Zison *et al*., 1977) has been revised and updated to include the assessment of toxic chemicals in the environment. The title has been changed to reflect the new content of the screening procedure.

1.2 PURPOSE AND SCOPE

This report contains a simplified methodology which can be used by planners or engineers to perform preliminary assessment of toxic and conventional pollutants in surface waters. Conventional pollutants include suspended sediments, nitrogen, phosphorus, coliform bacteria, BOD and dissolved oxygen deficits. The 129 EPA priority pollutants are included in the sections on toxic chemicals. The analyses require little external input, since much data are supplied by figures and tables in the text or appendices. Additional data can be found in Zison et al., 1978. All the algorithms are intended to be used on a desk-top calculator.

Where instructive, introductory material has preceded the actual presentation of water quality assessment methodologies. This was done to orient the planner toward pertinent background material, as well as to clearly state limitations of the methodologies due to assumptions and simplifications. Further, example calculations of the major emphases within each chapter are included to illustrate the ideas being presented. These examples are designed to unify the theory that has preceded it, as well as in some cases to introduce new but related ideas.

The units most commonly used in this report are those that historically appear in the literature. Often, the units are not metric. Consequently an english-metric-conversion appendix is included at the end of this report. Many equations are presented with both English and metric constants.

The report is divided into five major chapters (two through six). A brief description of the content of each chapter is presented in the following paragraphs.

- Chapter 2 deals with the environmental chemistry of toxic chemicals. Processes considered include photolysis, hydrolysis, volatilization, biodegradation and adsorption. The purpose of the chapter is to provide an understanding of the processes and to provide procedures for estimating associated rate and equilibrium constants.

- Chapter 3 deals with the estimation of pollutant loads from nonpoint and point sources for both toxic and conventional pollutants. Procedures include load estimation for single event and annual loads from agricultural, forested, and urban areas.

- In Chapter 4, impacts of point and nonpoint sources of conventional and toxic pollutants in rivers are addressed. Conventional pollutant interactions presented include BOD-DO, temperature, coliform bacteria, nutrients, and sediment transport. Fate of toxic chemicals is assessed using volatilization, sorption and first order degradation. Methods are also presented to handle large spills of toxic chemicals having density the same as or different from the receiving waters.

- Chapter 5 contains methods for assessing water quality in impoundments. The topics covered are sediment accumulation, thermal stratification, BOD-DO interactions, eutrophication, and fate of toxic materials. The physical/chemical processes governing the fate of toxicants as well as biological uptake and bioconcentration are considered.

- In Chapter 6, methods are presented for estuary classification, flushing time prediction, and transport of conservative and non-conservative pollutants and dissolved oxygen in well-mixed extuaries. For stratified estuaries, Pritchard's box model is used to determine the distribution of conservative materials. Additionally, methods are presented to calculate initial dilution from a waste water discharge and pollution distribution at the completion of and subsequent to initial dilution.

1.3 METHODOLOGY APPLICATION

For each category in the methodology, the six conceptual steps shown below should be followed to screen a river basin:

- obtain necessary tools and data to make calculations and utilize nomographs, etc.;
- identify problems that are obvious from inspection of the data base;
- determine the state variables which will be screened;
- apply procedures and compare where possible to observed data;
- consider consequences of errors; and
- reevaluate and make recommendations.

The techniques in the screening procedure are designed to interact which makes them ideal for use as an analytical tool for river basin surface waters which may include rivers, lakes, and/or estuaries. Although the procedures may interact, they can be applied individually and with identified data sets for specific case studies.

1.3.1 Base Maps

The first step in the screening process can be to obtain large scale topographic maps of the study area. These can be used to determine which water bodies are to be examined and to establish an order of study. Once this has been done, selected small scale (7 1/2-minute or 15-minute series) topographic sheets can be obtained. On these, the planner can locate and mark point source discharges, regions of specific kinds of land use, population centers, and industrial complexes. Use of overlays or push pins may be helpful in preparing these displays.

The maps are also very important in showing the relationships among water bodies and the flow patterns for stormwater runoff. Finally, control strategies may be displayed for examination on the maps.

1.3.2 Data Collection

Once the base maps are prepared, the kinds of data needed should be fairly clear in most cases. In general terms, the only data that will not be provided in this methodology are climatic and hydrologic data.

Hydrologic data includes such items as:

- Runoff quantity
- Stream flows (low flows, statistical flows such as 7Q10, critical flows to be protected as decreed by law)
- Inflows and outflows, stagnant regions, stratification, internal flow patterns
- Estuarine tidal prism

Much of the necessary hydrologic data will be available from the USGS, state geological surveys, state environmental protection agencies, and other governmental organizations. In addition, data may be available from the private sector, from universities, local citizens groups, and private firms.

Hydrologic data must usually be analyzed to serve as a basis for subsequent water quality analyses. Statistical methods may be applied to determine the annual runoff, monthly runoff, and critical flow for a stipulated return frequency, on a selected time basis.

To select critical flow, for example, one must have some base knowledge of the seasonal distribution of stream flow and quantity-quality relationships. In general, the summer low flow is considered as the critical condition for stream and estuarine analyses. Average annual runoff is to be used for lake analyses, even though wet years are generally more critical from the standpoint of lake water quality.

Climatic data may also be needed. Generally these are available from the National Climatic Center in Ashville, North Carolina. This agency can provide data summaries of various kinds for a large number of weather stations. Data include precipitation, cloud cover, humidity, and other important parameters. Computer tapes can often be provided.

In collecting data for the area to be screened, the Reach File data base (EPA, In Press) may also be useful. This data base contains information for over 68,000 river reaches in the 48 contiguous states. The Reach File provides a unique index for each of these river reaches and a systematic way of retrieving the hydrologic or water quality information which is available.

1.4 LIMITATIONS

The processes which govern the fate of pollutants in the environment are complex. A methodology such as this, designed for hand calculation, cannot be inclusive of all of these processes nor in all cases are the methods state-of-the-art. An attempt has been made in each chapter to cover the assumptions under which the algorithms are developed. Users should be aware of the assumptions, potential errors, and limitations of the tools presented. When deficiencies are noted or the methods deemed inappropriate, the user should be prepared to use a higher level analytical tool.

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CHAPTER 2

AQUATIC FATE OF TOXIC ORGANIC SUBSTANCES

2.1 INTRODUCTION

2.1.1 Background

Today's technological society generates enormous quantities of chemicals both as products for consumption and as waste. As the volume and number of chemicals has increased, numerous unintended adverse effects of these chemicals have been observed in the environment. Because of the potential hazard that exposure to these compounds poses to biota, the levels of toxic and carcinogenic substances in the environment have become important criteria for evaluating environmental quality.

The level, or concentration, of a toxic compound in the environment depends on the quantity added to the environment and the processes which influence its fate. "Transport" processes tend to distribute chemicals between the atmospheric, aquatic, and soil environments depending on the affinity of the compound for each phase. "Transformation" processes within each phase chemically alter pollutants to forms of lesser, equivalent, or sometimes greater toxicity. These processes occur at rates which are specific to each chemical and to each environmental compartment. The sum of these processes and their interactions, as Figure II-1 illustrates, determines the environmental fate and consequent exposure of biota to a toxic pollutant. The fate of toxic substances in the aquatic environment is the concern of this chapter.

2.1.2 Comparison of Conventional and Toxic Pollutants

Toxic substances frequently exhibit properties which are quite different from the properties of conventional aquatic pollutants. It is worthwhile to compare these differences in order to better appreciate the

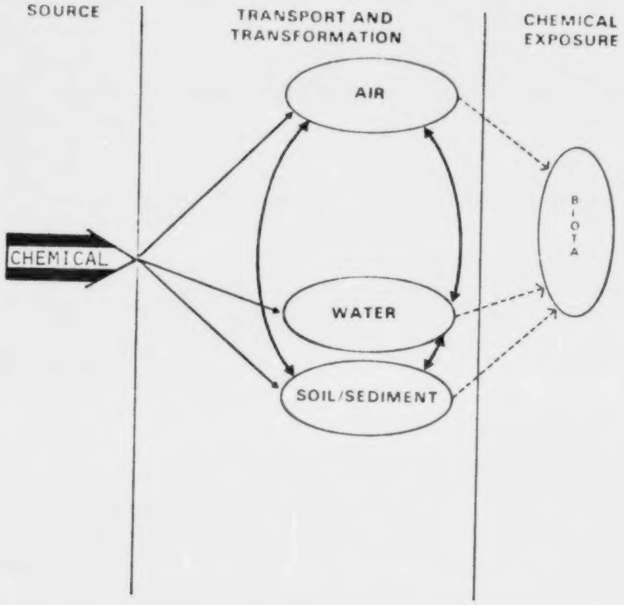

SOURCE
TRANSPORT AND TRANSFORMATION
CHEMICAL EXPOSURE
CHEMICAL
AIR
WATER
SOIL/SEDIMENT
BIOTA

FIGURE II-1 ENVIRONMENTAL FATE OF A TOXIC POLLUTANT (AFTER HAQUE, 1980)

problems of analyzing impacts of toxicants in surface water systems. Table II-1 shows some of the more important differences.

Typically, one to two dozen pollutants and water quality parameters are classified as "conventional". Until the past several years, these parameters (e.g. BOD, nutrients) have received most of the attention of water quality planners. In contrast to the small number of conventional pollutants there are thousands of toxicants and many more synthetic chemicals are continually being developed. Potentially, any of these toxicants could enter the environment.

TABLE II-1

BRIEF COMPARISON OF CONVENTIONAL AND TOXIC POLLUTANTS

Conventional	Toxic
One to two dozen pollutants fall into this category	Thousands fall into this category; many more being synthesized
Often large quantities required to produce impact (e.g. thousands lbs/day)	Small quantities can produce impact (e.g. few lbs/days)
Concentrations often expressed as ppm (mg/l)	Concentrations often expressed as ppb (μg/l), or in smaller units
Often travel in dissolved form	May be highly sorbed to suspended and bedded sediments
Mean residence time within water bodies often equal to or less than the mean residence time of moving waters	Can reside in bedded sediments for years
Many biodegrade into harmless substances	Many are transformed to chemicals which are also toxic; others are resistant to degradation and bioconcentrate

Even though there are relatively few types of conventional pollutants, numerous sources combine to routinely discharge large quantities. However, because many surface water bodies have a capacity to assimilate conventional pollutants (e.g. BOD) without apparent adverse effects, this practice is, within limits, both acceptable and pragmatic. Toxic substances, on the other hand, can cause adverse effects even at low discharge rates.

Concentrations of conventional pollutants are most often expressed in units of ppm (or mg/l). Because of the small quantities of toxicants which are typically released, concentrations are often expressed in the ppb (or μg/l) range, or in even smaller units. This represents at least a thousand fold difference relative to concentrations of conventional pollutants. However, because toxic substances present in small amounts can adversely impact the environment, these small concentrations can not always be ignored.

Many conventional pollutants are transported in dissolved form. The mean residence times of dissolved, conservative pollutants in a system is equivalent to the mean residence time of water in the system, which is:

- the hydraulic detention time for freshwater lakes
- the travel time for freshwater rivers; and
- the flushing time for estuaries.

Many toxic chemicals strongly sorb to suspended and bedded sediments and consequently can become a part of the immobile sediments in the bed. The residence time of such chemicals can be on the order of years. Therefore, depending on the properties of the toxicant the period of impact can greatly exceed the period of discharge (e.g. a PCB spill may occur in a few minutes, but quantities of the PCB may remain in immobile, bedded, sediments for years). Consequently the recovery period of a system can be years.

2.1.3 Water Quality Criteria

As previously indicated, toxicants are present in the environment in quantities which are often measured in the ppb range. Such small concentrations are often foreign to many workers in the field. When data or model predictions contain concentrations in the ppb range, the significance of the toxicant level is not always obvious (i.e. there is no "feel" as to whether the concentration is large or small). Proposed criteria for toxic substances can serve as a basis to gauge the significance of observed or predicted levels. Table II-2 shows proposed criteria for numerous toxicants. Since proposed criteria evolve over time the criteria shown in the table are not necessarily the most current. Nevertheless, their function remains: to provide a comparison with levels observed or predicted in real systems. The data in these tables come from the "Red Book" (U.S. EPA, 1976) and the Federal Register, March 15, 1979; July 25, 1979; October 1, 1979; and November 28, 1980. Criteria, designed to protect human health, for levels of toxicants in domestic water supplies, are available from these same sources as well.

2.1.4 Frequency of Discharge of Toxic Substances from Industries

Numerous organizations, including the U.S. Department of Transportation and the U.S. Environmental Protection Agency, continually collect and analyze data on the discharge of toxic substances. Table II-3 summarizes the results of a study reported by Keith and Telliard (1979) which shows the frequency of detection of the 129 priority pollutants in industrial wastewaters. A total of 32 industrial categories were analyzed for organics and 28 for metals. The number of samples ranged from 2532 to 2988. Table II-4 summarizes the most commonly discharged priority pollutants. Table III-53, shown in the next chapter, provides a breakdown by industry of the occurrence of priority pollutants in industrial effluent.

It is common in this country for numerous industrial plants to release their effluent into a single water body. Because of this situation a question that naturally arises is: Based on the number and type of industries located on the water body, what kinds of toxic chemicals are likely to be discharged there ? If the industrial categories of each plant

TABLE II-2
PROPOSED CRITERIA FOR TOXIC SUBSTANCES DESIGNATED TO PROTECT AQUATIC LIFE

COMPOUND	Freshwater 24 Hour Average µg/l	Freshwater Maximum µg/l	Freshwater "Red Book" µg/l	Saline water 24 Hour Average µg/l	Saline water Maximum µg/l	Saline water "Red Book" µg/l
Acenaphthene	LD[a]	1700[b]		710[c]	970[b]	
Acrolein	21[c]	68[b]		LD	55[b]	
Acrylonitrile	2600[c]	7550[b]		LD	LD	
Aldrin/Dieldrin	0.0019	2.5	0.003	0.0019	0.71	0.003
Antimony	1600	9000		LD	LD	
Arsenic	40[c]	440[b]		LD	508[b]	
Asbestos	LD	LD		LD	LD	
Benzene	LD	5300[b]		700[c]	5100[b]	
Benzidine	LD	2500		LD	LD	
Beryllium	5.3[c]	130[b]	11.-1100	LD	LD	
Cadmium	d	e	0.4-1.2[f] 4.0-12.0[g]	4.5	59	5.0
Carbon Tetrachloride	620	1400		2000	4000	
Chlordane	0.0043	2.4	0.01	0.0040	0.09	0.004
Chlorinated benzenes						
Chlorobenzene	1500[h]	3500[h]		120[h]	280[h]	
1,2,4 - Trichlorobenzene	210[h]	470[h]		3.4[h]	7.8[h]	
1,2,3,5 - Tetrachlorobenzene	170[h]	390[h]		2.6[h]	5.9[h]	
1,2,4,5 - Tetrachlorobenzene	97[h]	220[h]		9.6	26	
Pentachlorobenzene	16[h]	36[h]		1.3[h]	2.9[h]	
Chlorinated Ethanes						
1,2 - Dichloroethane	3900[h]	8000[h]		880[h]	2000[h]	
1,1,1 - Trichloroethane	5300[h]	12000[h]		240[h]	540[h]	
1,1,2 - Trichloroethane	310[h]	710[h]		LD	LD	
1,1,1,2 - Tetrachloroethane	420[h]	960[h]		LD	LD	
1,1,2,2 - Tetrachloroethane	170[h]	380[h]		70[h]	160[h]	
Pentachloroethane	440[h]	1000[h]		38	87	
Hexachloroethane	62[h]	140[h]		7.0[h]	16[h]	
Chlorinated Naphthalenes	29	67		2.8	6.4	
Chlorinated Phenols						
4 - Chlorophenol	45	180		LD	LD	
2,4,6 - Trichlorophenol	52	150		LD	LD	
Chloroalkyl Ethers	LD	LD		LD	LD	
Chloroform	500	1200		620[h]	1400[h]	
2 - Chlorophenol	60	180		LD	LD	
Chromium (Hexavalent)	0.29	21	100	18	1260	
Copper	5.6	i	j	4.0	23	j
Cyanide	3.5	52	5.0	LD	LD	5.0
DDT	0.00023	0.41	.001	0.0067[h]	0.021[h]	.001
Dichlorobenzenes						
1,2 - Dichlorobenzene	44	99		15[h]	34[h]	
1,3 - Dichlorobenzene	310[h]	700[h]		22[h]	49[h]	
1,4 - Dichlorobenzene	190[h]	440[h]		15[h]	34[h]	

TABLE II-2 (Continued)

COMPOUND	Freshwater 24 Hour Average µg/l	Freshwater Maximum µg/l	Freshwater "Red Book" µg/l	Saline Water 24 Hour Average µg/l	Saline Water Maximum µg/l	Saline Water "Red Book" µg/l
3,3' - Dichlorobenzidine	LD	LD		LD	LD	
Dichloroethylenes						
1,1 - Dichloroethylene		11600		224000		
1,2 - Dichloroethylene		11600		224000		
2,4 - Dichlorophenol	0.4	110		LD	LD	
Dichloropropanes and Dichloropropenes						
1,1 - Dichloropropane	410	930		LD	LD	
1,2 - Dichloropropane	920	2100		400^h	910^h	
1,3 - Dichloropropane	4800	11000		79	180	
1,3 - Dichloropropene	18	250		5.5^h	14^h	
2,4 - Dimethylphenol	38	86		LD	LD	
Dinitrotoluenes						
2,3 - Dinitrotoluene	12	27		4.4^h	10^h	
2,4 - Dinitrotoluene	620	1400		LD	LD	
1,2 - Diphenylhydrazine	17	38		LD	LD	
Endosulfan	0.042	0.49	0.003	LD	LD	0.001
Endrin	0.0023	0.18	0.004	0.0023	0.037	0.004
Enthylbenzene	LD	LD		LD	LD	
Fluoranthene	250^h	560^h		0.30	0.69	
Haloethers						
4 - bromophenylphenyl ether	6.2	14		LD	LD	
Halomethanes						
Chloromethane	7000	16000		3700^h	8400^h	
Bromomethane	140	320		170^h	380^h	
Dichloromethane	4000^h	9000^h		1900^h	4400^h	
Tribromomethane	840^h	1900^h		180	420	
Heptachlor	0.0038	0.52	0.001	0.0036	0.053	0.001
Hexachlorobutadiene	LD	LD		LD	LD	
Hexachlorocyclohexane						
Lindane	0.080	2.0		LD	0.16	
Other isomers	LD	LD		LD	LD	
Hexachlorocyclopentadiene	0.39	7.0		LD	LD	
Isophorone	2100	4700		97	220	
Lead	k	l	m	25^b	668^b	
Mercury (total)	0.2	4.1	0.05	0.10	3.7	0.10
Naphthalene	LD	LD		LD	LD	
Nickel	n	o	p	7.1	140	p
Nitrobenzene	480	1100		53	120	

TABLE II-2 (Continued)

	Freshwater			Saline Water		
COMPOUND	24 Hour Average µg/l	Maximum µg/l	"Red Book" µg/l	24 Hour Average µg/l	Maximum µg/l	"Red Book" µg/l
Nitrophenols						
2 - Nitrophenol	2700[h]	6200[h]		LD	LD	
4 - Nitrophenol	240[h]	550[h]		53	120	
2,4 - Dinitrophenol	79[h]	180[h]		37[h]	84[h]	
2,4 - Dinitro-6-methylphenol	57[h]	140[h]		LD	LD	
2,4,6 - Trinitrophenol	1500[h]	3400[h]		150[h]	340[h]	
N-Nitrosodiphenylamine	LD	LD		LD	LD	
Pentachlorophenol	6.2	14		3.7	8.5	
Phenol	600	3400		LD	LD	
Phthalate esters	LD	LD	3.0	LD	LD	
Polychlorinated biphenyls	0.014	2.0[b]	0.001	0.030	10[b]	0.001
Polynuclear aromatic hydrocarbons	LD	LD		LD	LD	
Selenium	35	260	p	54	410	p
Silver	0.0090	1.9	p	0.26	2.3	p
2,3,7,8 - Tetrachlorodibenzo-p-dioxin	LD	LD				
Tetrachloroethene	310	700		79	180	
Thallium	LD	LD		LD	LD	
Toluene	2300[h]	5200[h]		100	230	
Toxaphene	0.013	1.6	0.005	LD	0.07	0.005
Trichloroethene	1500	3400		LD	LD	
Vinyl chloride	LD	LD		LD	LD	
Zinc	47	q	p	58	170	

[a] LD denotes lack of data.

[b] Acute toxicity level.

[c] Chronic toxicity level.

[d] The value in µg/l should not exceed exp [1.05 ln (hardness) -8.53] where hardness is expressed in mg/l as $CaCO_3$.

[e] The value in µg/l should not exceed exp [1.05 ln (hardness) -3.73] where hardness is expressed in mg/l as $CaCO_3$

[f] 0.4 mg - 1.2 mg/l for cladocerans and salmonid fishes

[g] 4.0 mg -12.0 mg/l for other, less sensitive aquatic life.

[h] Values derived using procedures other than the guidelines.

[i] The value in µg/l should not exceed exp [0.94 ln (hardness -1.23)] ,where hardness is expressed in mg/l as $CaCO_3$.

[j] For freshwater and marine aquatic life, 0.1 times a 96 hr LC_{50} as determined through nonaerated biossay using a sensitive aquatic resident species.

[k] The value in µg/l should not exceed exp [2.35 ln (hardness) -9.48] where hardness is expressed in mg/l as $CaCO_3$.

[l] The value in µg/l should not exceed exp [1.22 ln (hardness) -0.47] where hardness is expressed in mg/l as $CaCO_3$.

[m] 0.01 times the 96 hour LC_{50} value, using the receiving or comparable water as the diluent and soluble lead measurements (using an 0.45 micron filter) for sensitive freshwater resident species.

[n] The value in ug/l should not exceed exp [0.76 ln (hardness)+1.06] where hardness is expressed in mg/l as $CaCO_3$.

[o] The value in µg/l should not exceed exp [0.76 ln (hardness)+4.02] where hardness is expressed in mg/l as $CaCO_3$.

[p] For marine and/or fresh water aquatic life, 0.01 of the 96 hour LC_{50} as determined through bioassay using a sensitive resident species.

[q] The value in ug/l should not exceed exp [0.33 ln (hardness) + 1.95] where hardness is expressed in mg/l as $CaCO_3$.

The criteria in this Table are from the following sources:

- "Red Book" (U.S.EPA 1976)
- Federal Register on these dates:
  March 15, 1979 - July 25, 1979 - October 1, 1979 - November 28, 1980

TABLE II-3
EPA LIST OF 129 PRIORITY POLLUTANTS AND THE RELATIVE FREQUENCY OF THESE MATERIALS IN INDUSTRIAL WASTEWATERS
(After Keith and Telliard, 1979)

Percent of Samples[a]	Number of Industrial Categories[b]		Percent of Samples[a]	Number of Industrial Categories[b]	
		Purgeable Organics			
1.2	5	Acrolein	2.1	5	1,2-Dichloropropane
2.7	10	Acrylonitrile	1.0	5	1,3-Dichloropropene
29.1	25	Benzene	34.2	25	Methylene chloride
29.3	28	Toluene	1.9	6	Methyl chloride
16.7	24	Ethylbenzene	0.1	1	Methyl bromide
7.7	14	Carbon tetrachloride	1.9	12	Bromoform
5.0	10	Chlorobenzene	4.3	17	Dichlorobromomethane
6.5	16	1,2-Dichloroethane	6.8	11	Trichlorofluoromethane
10.2	25	1,1,1-Trichloroethane	0.3	4	Dichlorodifluoromethane
1.4	8	1,1-Dichloroethane	2.5	15	Chlorodibromomethane
7.7	17	1,1-Dichloroethylene	10.2	19	Tetrachloroethylene
1.9	12	1,1,2-Trichloroethane	10.5	21	Trichloroethylene
4.2	13	1,1,2,2-Tetrachloroethane	0.2	2	Vinyl chloride
0.4	2	Chloroethane	7.7	18	1,2-trans-Dichloroethylene
1.5	1	2-Chloroethyl vinyl ether	0.1	2	bis(Chloromethyl)ether
40.2	28	Chloroform			
		Base/Neutral Extractable Organic Compounds			
6.0	9	1,2-Dichlorobenzene	5.7	11	Fluorene
		1,3-Dichlorobenzene	7.2	12	Fluoranthene
		1,4-Dichlorobenzene	5.1	9	Chrysene
0.5	5	Hexachloroethane	7.8	14	Pyrene
0.2	1	Hexachlorobutadiene	10.6	16	Phenanthrene
1.1	7	Hexachlorobenzene			Anthracene
1.0	8	1,2,4-Trichlorobenzene	2.3	6	Benzo(a)anthracene
0.4	3	bis(2-Chloroethoxy)methane	1.6	6	Benzo(b)fluoranthene
10.6	18	Naphthalene	1.8	6	Benzo(k)fluoranthene
0.9	9	2-Chloronaphthalene	3.2	8	Benzo(a)pyrene
1.5	13	Isophorone	0.8	4	Indeno(1,2,3-c,d)pyrene
1.8	9	Nitrobenzene	0.2	4	Dibenzo(a,h)anthracene
1.1	3	2,4-Dinitrotoluene	0.6	7	Benzo(g,h,i)perylene
1.5	9	2,6-Dinitrotoluene	0.1	2	4-Chlorophenyl phenyl ether
0.04	1	4-Bromophenyl phenyl ether	0	0	3,3'-Dichlorobenzidine
41.9	29	bis(2-Ethylhexyl)phthalate	0.2	4	Benzidine
6.4	12	Bi-*n*-octyl phthalate	1.1	4	bis(2-Chloroethyl)ether
5.8	15	Dimethyl phthalate	0.8	7	1,2-Diphenylhydrazine
7.6	20	Diethyl phthalate	0.1	1	Hexachlorocylclopentadiene
18.9	23	Di-*n*-butyl phthalate	1.2	5	N-Nitrosodiphenylamine
4.5	12	Acenaphthylene	0.1	1	N-Nitrosodimethylamine
4.2	14	Acenaphthene	0.1	2	N-Nitrosodi-*n*-propylamine
8.5	13	Butyl benzyl phthalate	1.4	6	bis(2-Chloroisopropyl)ether
		Acid Extractable Organic Compounds			
26.1	25	Phenol	1.9	8	*p*-Chloro-*m*-cresol
2.3	11	2-Nitrophenol	2.3	10	2-Chlorophenol
2.2	9	4-Nitrophenol	3.3	12	2,4-Dichlorophenol
1.6	6	2,4-Dinitrophenol	4.6	12	2,4,6-Trichlorophenol
1.1	6	4,6-Dinitro-o-cresol	5.2	15	2,4-Dimethylphenol
6.5	18	Pentachlorophenol			
		Pesticides/PCB's			
0.3	3	α-Endosulfan	0.3	3	Heptachlor
0.4	4	β-Endosulfan	0.1	1	Heptachlor epoxide
0.2	2	Endosulfan sulfate	0.2	4	Chlordane
0.6	4	α-BHC	0.2	2	Toxaphene
0.8	6	β-BHC	0.6	2	Aroclor 1016
0.2	4	δ-BHC	0.5	1	Aroclor 1221
0.5	3	γ-BHC	0.9	2	Aroclor 1232
0.5	5	Aldrin	0.8	3	Aroclor 1242
0.1	3	Dieldrin	0.6	2	Aroclor 1248
0.04	1	4,4'-DDE	0.6	3	Aroclor 1254
0.1	2	4,4'-DDD	0.5	1	Aroclor 1260
0.2	2	4,4'-DDT	-	-	2,3,7,8-Tetrachlorodibenzo-*p*-dioxin (TCDD)
0.2	3	Endrin			
0.2	2	Endrin aldehyde			
		Metals			
18.2	20	Antimony	16.5	20	Mercury
19.9	19	Arsenic	34.7	27	Nickel
14.1	18	Beryllium	18.9	21	Selenium
30.7	25	Cadmium	22.9	25	Silver
53.7	28	Chromium	19.2	19	Thallium
55.5	28	Copper	54.6	28	Zinc
43.8	27	Lead			
		Miscellaneous			
33.4	19	Total cyanides	Not available		Asbestor (fiborous)
			Not available		Total phenols

---

[a] The percent of samples represents the number of times this compound was found in all samples in which it was analyzed for divided by the total as of 31 August 1978. Numbers of samples ranged from 2532 to 2998 with the average being 2617.

[b] A total of 32 industrial categories and subcategories were analyzed for organics and 28 for metals as of 31 August 1978.

TABLE II-4

MOST COMMONLY DISCHARGED PRIORITY POLLUTANTS

Non-Metals

Pollutant	Percent of Samples	Percent of Industries
Bis (2-Ethylhexyl) Phthalate	41.9	91
Chloroform	40.2	88
Methylene Chloride	34.2	78
Total Cyanides	33.4	59
Toluene	29.3	88
Benzene	29.1	78
Phenol	29.1	78
Di-*n*-Butyl Phthalate	18.9	72
Ethylbenzene	16.7	75
Naphthalene	10.6	56
Phenanthrene and Anthracene	10.6	50

Metals

Pollutant	Percent of Samples	Percent of Industries
Copper	55.5	100
Zinc	54.6	100
Chromium	53.7	100
Lead	43.8	96
Nickel	34.7	96

are known, the probability that a particular pollutant is discharged from at least one of the plants is:

$$P_j = 1 - \prod_{i=1}^{n} \left(1 - \frac{f_{ij}}{100}\right) \quad j = 1, M \qquad \text{(II-1)}$$

where

f_{ij} = relative frequency of discharge of pollutant type j from plant type i, expressed as a percent

P_j = probability that pollutant type j is discharged from at least one of the n plants located on the water body.

M = number of toxic substances being analyzed

If the industrial categories of the plants are not known, then the probability that a particular pollutant is discharged can be estimated using Table II-3 together with the following formula:

$$P_j = 1 - \left(1 - \frac{g_j}{100}\right)^n \quad j = 1,M \qquad \text{(II-2)}$$

where

g_j = percent of samples containing pollutant j

P_j = probability that pollutant j is detected in at least one of the n discharges.

Equation II-1 is obviously the more accurate of the two formulae, because it is based on a knowledge of the types of industries which discharge. Although the above equations provide information on the likelihood that different chemicals are discharged into the environment, and thus can be used to prioritize investigative efforts, they do not predict quantities of pollutants which are discharged. Chapter III can be used to generate that type of information.

2.1.5 Physical and Chemical Characteristics of Toxic Organic Compounds

The most intensively investigated toxic pollutants, as a group, are the priority pollutants. Because of the greater availability of data on priority pollutants from such sources as Callahan et al. (1979), Dilling et al. (1975), and Mackay and Leinonen (1975), data are presented for organic priority pollutants in the following categories:

- Halogenated Aliphatic Hydrocarbons (Table II-5)
- Pesticides (Table II-6)
- Polychlorinated Biphenyls (Table II-7)
- Monocyclic Aromatic Hydrocarbons (Table II-8)
- Polycyclic Aromatic Hydrocarbons (Table II-9)

The properties of the pollutants tabulated in Tables II-5 through II-9 are:

- Vapor pressure, Torr (1 Torr = 1 mm-Hg)
- Solubility
- Octanol-water partition coefficient (K_{ow})
- Volatilization half-life
- Qualitative statement of the importance of sorption.

Specific information is included in the tables for volatilization and sorption because of the demonstrated importance of these processes in governing the fate of many pollutants. In particular, for the approximately 103 organic priority pollutants:

- Sorption processes are important for 60
- Sorption is not important for 28
- It is not certain if sorption is important for the remaining 15
- Volatilization is important for 52
- Volatilization is not important for 44
- It is uncertain if volatilization is important for the remaining 7.

The volatilization half-lives presented in the tables were typically measured under a specific set of laboratory conditions, and consequently are shorter than in most natural systems. Other useful properties such as

TABLE II-5
SELECTED CHARACTERISTICS OF VARIOUS ALIPHATIC HYDROCARBONS

Halogenated Aliphatic Hydrocarbons	Vapor Pressure (Torr) at 20°C	Solubility	K_{ow}	Volatilization Half-Life	Sorption Important?
Chloromethane	3700	6450-7250 mg/l at 20°C	8	27 minutes[a]	No
Dichloromethane	362	13000-20000 mg/l at 25°C	20	21 minutes[a]	Probably Not
Trichloromethane (chloroform)	150	8200 mg/l at 20°C	93	21 minutes[a]	Probably Not
Tetrachloromethane (carbon tetrachloride)	90	785 mg/l at 20°C	400	29 minutes[a]	Uncertain
Chloroethane	1000	5740 mg/l at 20°C	35	21 minutes[a]	Probably Not
1,1-Dichloroethane	180	5500 mg/l at 20°C	60	22 minutes[a]	Probably Not
1,2-Dichloroethane	61	8690 mg/l at 20°C	30	29 minutes[a]	Probably Not
1,1,1-Trichloroethane	96	440-4400 mg/l at 20°C	150	20 minutes[a]	Probably Not
1,1,2-Trichloroethane	19	4500 mg/l at 20°C	150	21 minutes[a]	Uncertain
1,1,2,2-Tetrachloroethane	5	2900 mg/l at 20°C	360	56 minutes[a]	Uncertain
Hexachloroethane	0.4	50 mg/l at 22°C	2200	45 minutes[a]	Uncertain
Chloroethene (vinyl chloride)	2660	60 mg/l at 10°C	4	26 minutes[a]	Probably Not
1,1-Dichloroethene	591	400 mg/l at 20°C	30	22 minutes[a]	Probably Not
1,2-*trans*-Dichloroethene	200	600 mg/l at 20°C	30	22 minutes[a]	Probably Not
Trichloroethene	57.9	1100 mg/l at 20°C	200	21 minutes[a]	Probably Not
Tetrachloroethene	14	150-200 mg/l	760	26 minutes[a]	Probably Not
1,2-Dichloropropane	42	2700 mg/l	190	<50 minutes[a]	Probably
1,3-Dichloropropene	25	2700 mg/l	95	31 minutes[a]	Uncertain
Hexachlorobutadiene	0.15	2	5500	-	Probably
Hexachlorocyclopentadiene	0.081 at 25°C	0.8 mg/l	10^4	-	Probably
Bromomethane	1420	900 mg/l	10	~30 minutes	Probably Not
Bromodichloromethane	50	-	75	-	Uncertain
Dibromochloromethane	15	-	120	-	Uncertain
Tribromomethane	10	3000 mg/l	200	-	Uncertain
Dichlorodifluoromethane	4306	280 mg/l	145	few minutes	Probably
Trichlorofluoromethane	667	1100 mg/l	3400	few minutes	Uncertain

[a] Stirring in an open container of depth 65 mm at 200 RPM (Dilling *et al.*, 1975)

TABLE II-6

VARIOUS CHARACTERISTICS OF SELECTED PESTICIDES

Pesticide	Vapor Pressure (Torr)	Solubility	K_{ow}	Volatilization Half-Life[a]	Sorption Important?
Acrolein	220 at 20°C 330 at 30°C	20.8% at 20°C	0.8	Uncertain	No
Aldrin	2.3×10^{-5} at 20°C 6×10^{-6} at 25°C	17-180 ppb at 25°C	≈410	Few hours to few days	Yes
Chlordane	1×10^{-5} at 25°C	0.056-1.85 ppm	600	Several weeks	Probably
DDD	$10.2\text{-}18.9\times10^{-7}$ at 30°C	20-100 ppb at 25°C	10^{6}	1 day to 1 month	Yes
DDE	$6.2\text{-}6.5\times10^{-6}$ at 20°C	1.2-140 ppb at 20°C	5×10^{5}	1 to 10 hours	Yes
DDT	1.5×10^{-7} at 20°C 1.9×10^{-7} at 25°C	2-85 ppb	$10^{4}\text{-}10^{6}$	4 hours-1 week	Yes
Dieldrin	1.8×10^{-7} to 2.9×10^{-7} at 20°C	186-200 ppb at 25°C	-	Few hours to few days	Probably
Endosulfan	1×10^{-5} at 25°C	100-260 ppb at 20°C	4×10^{3}	11 days-1 year	Yes
Endrin	2×10^{-7}	220 ppb at 25°C	4×10^{5}	-	Uncertain
Heptachlor	3×10^{-4}	56-180 ppb at 25°C	-	-	Probably
Heptachlor Epoxide	-	200-350 ppb at 25°C	-	-	Probably
Hexachlorocyclohexane	$10^{-5}\text{-}10^{-7}$	0.70-21.3 ppm at 25°C	10^{4}	-	Probably
Lindane	$10^{-4}\text{-}10^{-6}$	5-12 ppm at 25°C	5×10^{3}	100-200 days	Probably
Isophorone	0.38	12000 ppm	50	Probably great	No
TCDD	-	0.2 ppb	-	-	Yes
Toxaphene	0.2-0.4	0.7-3. ppm	2000	-	Yes

[a] Conditions described in Callahan *et al*. (1979)

TABLE II-7

SELECTED CHARACTERISTICS OF POLYCHLORINATED BIPHENYLS AND RELATED COMPOUNDS

PCBs and Related Compounds	Percent Chlorine	Density (gm/cm^3)	Vapor Pressure at 25 C°(Torr)	Solubility mg/l	K_{OW}	Volatilization	
						Half-Lives in laboratory (hrs)[a]	Loss in Natural Systems[b]
Aroclor 1016	41	1.33	$4x10^{-4}$	0.42	$2x10^4$-$3x10^5$	9.9	3.6% after 24 hours
Aroclor 1221	21	1.15	$6.7x10^{-3}$	15.	600-10^4	-	4.2% after 24 hours
Aroclor 1232	32	1.24	$4x10^{-3}$	1.45	$1.5x10^3$-$3x10^4$	-	-
Aroclor 1242	42	1.35	$4x10^{-4}$	0.1-0.3	10^4-$4x10^5$	12.1	-
Aroclor 1248	48	1.41	$4.9x10^{-4}$	0.054	$\sim 10^6$	9.5	-
Aroclor 1254	54	1.50	$7.7x10^{-5}$	0.01-0.06	$\sim 10^6$	10.3	-
Aroclor 1260	60	1.58	$4x10^{-5}$	0.0027	$>10^6$	10.2	34%-67% after 12 weeks
2-chloronaphthalene	-	-	0.017	6.47	10^4	-	

[a] At 25°C in 1 m^3 of water, 1 m deep (MacKay and Leinonen, 1975).

[b] Conditions described in Callahan et al. (1979)

TABLE II-8

SELECTED CHARACTERISTICS OF MONOCYCLIC AROMATIC HYDROCARBONS

Monocyclic Aromatics	Vapor Pressure (Torr)	Solubility	K_{ow}	Volatilization Half-Life	Sorption Important?
Benzene	95. at 25°C	1800 mg/l at 25°C	100	4.8 hrs at 25°C[a]	Uncertain
Chlorobenzene	~10 at 20°C	~500 mg/l	700	0.5-9 hrs	Probably
1,2-Dichlorobenzene	1.5 at 25°C	145 mg/l	2400	8-9 hours[a]	Probably
Hexachlorobenzene	10^{-5} at 20°C	~20 μg/l	~10^{6}	8 hours[a]	Yes
Ethylbenzene	7	152 mg/l	1400	5-6 hours[a]	Probably
Toluene	29 at 25°C	535 mg/l	500	5 hours[a]	Probably
2,4-Dinitrotoluene	0.001 at 59°C	270 mg/l at 22°C	100	~100 days	Yes
2,6-Dinitrotoluene	low	~300 mg/l	100	~100 days	Yes
Pentachlorophenol	0.0001	14 mg/l	10^{5}	>100 days	Yes
2-Nitrophenol	1.0 at 49°C	2100 mg/l at 20°C	60	-	Yes
4-Nitrophenol	2.2 at 146°C	16000 mg/l at 25°C	80	-	Yes
2,4-Dinitrophenol	-	5600 mg/l	34	-	Yes
4,6-Dinitro-o-cresol	-	-	700	-	Yes

[a] Mackay and Leinonen (1975). Calculated based on water depth of 1 m, and using mass transfer coefficients of 20 cm/hr and 3000 cm/hr for the liquid and gas transfer phases, respectively.

TABLE II-9

SELECTED CHARACTERISTICS OF VARIOUS POLYCYCLIC AROMATIC HYDROCARBONS

Polycyclic Aromatics	Vapor Pressure (Torr)	Solubility	K_{ow}	Volatilization Important?	Sorption Important?
Acenaphthene	10^{-3}-10^{-2} at 20°C	3.4 mg/l at 25°C	21,000	Less than sorption	Yes
Acenaphthylene	10^{-3}-10^{-2} at 20°C	3.93 mg/l	12,000	Less than sorption	Yes
Flourene	10^{-3}-10^{-2} at 20°C	1.9 mg/l	15,000	Less than sorption	Yes
Naphthalene	.0492	32. mg/l	2,300	Less than sorption	Yes
Anthracene	$2x10^{-4}$ at 20°C	0.05-0.07 mg/l at 25°C	28,000	Probably	Yes
Fluoranthrene	10^{-6} to 10^{-4} at 20°C	0.26 mg/l at 25°C	340,000	Probably Not	Yes
Phenanthrene	$6.8x10^{-4}$ at 20°C	1.0-1.3 mg/l at 25°C	29,000	Probably Not	Yes
Benzo[a]anthracene	$5x10^{-9}$ at 20°C	0.01 mg/l at 25°C	$4x10^{5}$	No	Yes
Benzo[b]fluoranthrene	11^{-11} to 10^{-6} at 20°C	-	$4x10^{6}$	Probably Not	Yes
Benzo[k]fluoranthrene	$9.6x10^{-11}$ at 20°C	-	$7x10^{6}$	Probably Not	Yes
Chrysene	10^{-11} to 10^{-6} at 20°C	0.002 mg/l at 25°C	$4x10^{5}$	Probably Not	Yes
Pyrene	$6.9x\ 0^{-7}$ at 20°C	0.14 mg/l at 25°C	$2x10^{5}$	Probably Not	Yes
Benzo[ghi]perylene	$\sim 10^{-10}$	0.00026 mg/l at 25°C	10^{7}	Probably Not	Yes
Benzo[a]pyrene	$5x10^{-9}$	0.0038 mg/l at 25°C	10^{6}	Probably Not	Yes
Dibenzo[a]anthracene	$\sim 10^{-10}$	0.0005 mg/l at 25°C	10^{6}	Probably Not	Yes
Indeno[1,2,3-cd]pyrene	$\sim 10^{-10}$	-	$5x10^{7}$	Probably Not	Yes

molecular weight and specific gravity are available in standard references such as Perry and Chilton (1973).

2.1.6 Scope and Organization of Chapter

The complexity of the transport and transformation processes which influence the fate of toxicants require additional analytical tools beyond those required for conventional pollutants. This chapter develops these analytical tools in a general way that is applicable to rivers, lakes, and estuaries. Individual chapters on the various surface water types refine these tools further and provide a framework within which to use them. When used together, the various chapters in this document should help the user both understand and quantitatively represent the processes influencing the aquatic fate of a pollutant.

This chapter presents both a general overview of the screening approach for toxicants and a detailed description of the processes included in the screening methodology. The various topics are organized as follows:

- Screening Methods for Toxic Organic Substances
- Speciation Processes
    1) Acid-base Effects
    2) Sorption
- Transport Processes
    1) Solubility Limits
    2) Volatilization
- Transformation Processes
    1) Biodegradation
    2) Photolysis
    3) Hydrolysis

These methods apply primarily to the fate of toxic organic substances. Some processes act on metals as well, but considerable expansion of the material would be necessary to incorporate them in these screening methods. Generally, the complexity of the environmental chemistry of metals makes them more difficult to handle with simple methods. The utility of these methods remain high even without metals since the overwhelming majority of toxic substances and over 100 of the 129 EPA Priority Pollutants are organic compounds. In lieu of procedures designed specifically for metals, the user may apply the screening methods for conservative substances. The advantages and limitations of this approach are discussed in Section 2.2.2.2.

2.2 SCREENING METHODS FOR TOXIC ORGANIC COMPOUNDS

2.2.1 Modeling the Fate of Toxic Organics

The goal of this screening methodology for toxic pollutants is to help the user identify surface water bodies where toxicants could reach hazardous levels. Multiple approaches for identifying pollution problems are possible, e.g. extensive field measurements, statistical correlations of discharges and pollutants detected in rivers, computer simulation models, etc. The approach taken here is to present simple methods for assessing the fate of toxicants.

The application of any method necessitates the use of judgment on the part of those applying it. In almost every case, the user must estimate many of the methods' input parameters on the basis of limited data. Consequently, even the projections of detailed computer models such as EXAMS (Burns, et al., 1981) and PEST (Park, et al., 1980) are only as good as the accuracy of the assumptions made by their developers and users. Thus, the goal of the materials presented herein is twofold: to present simple methods and to provide the background necessary to make knowledgeable judgments.

Predicting aquatic fate of pollutants involves several steps. The steps described in the remainder of this section include:

- Determination of Fate-Influencing Processes
- Delineation of Environmental Compartments
- Representation of Hydrologic Flow
- Mathematical Representation of Speciation Processes
- Mathematical Representation of Transport and Transformation Processes
- Determination of Pollutant Load and Mode of Entry into the Aquatic Environment

Prediction of the fate of toxic pollutants requires the user to know which processes act on the toxicant. Figure II-2 illustrates the transport and transformation processes which are of potential importance in a lake or

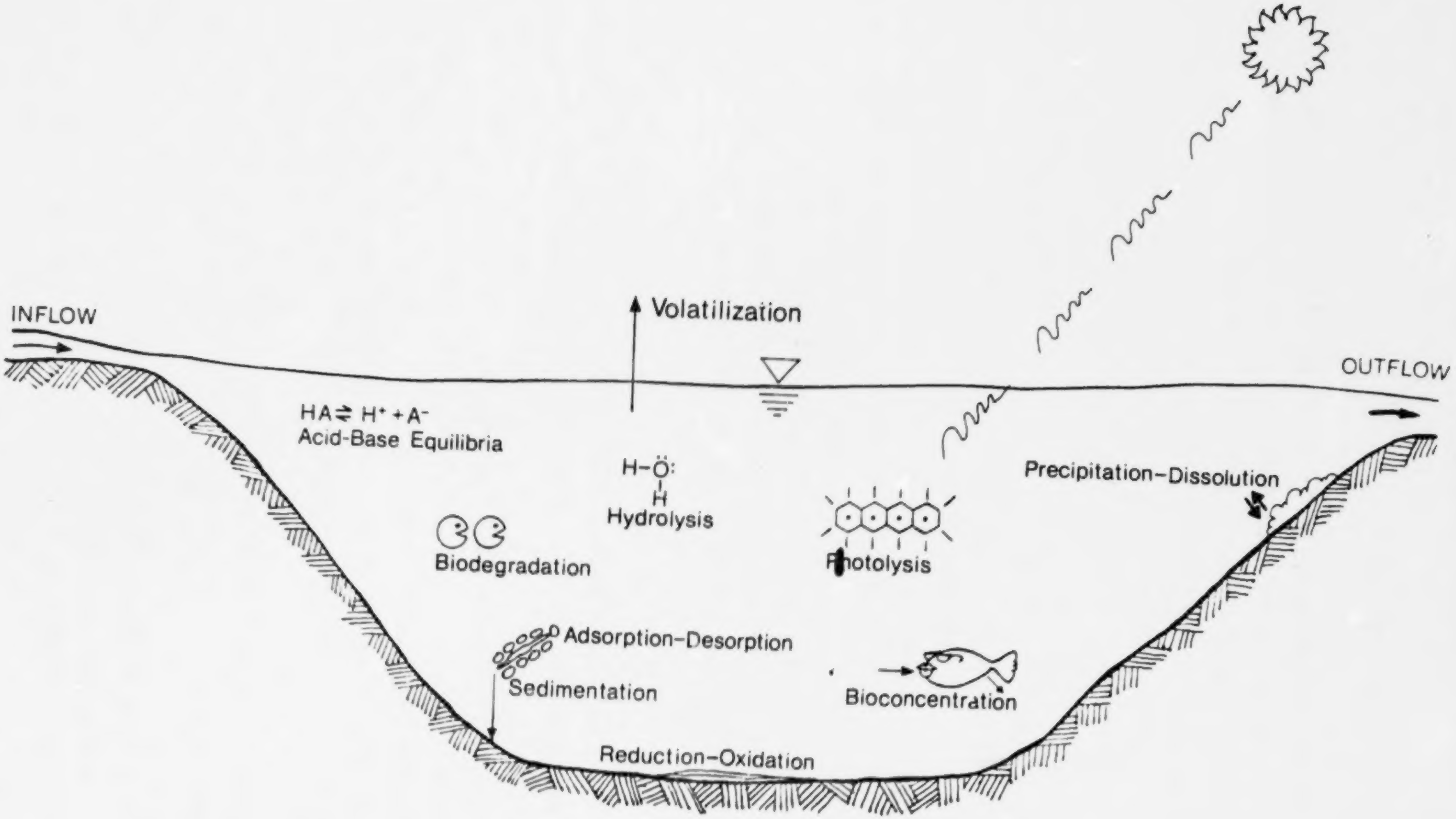

INFLOW
Volatilization
OUTFLOW
HA ⇌ H⁺ + A⁻
Acid-Base Equilibria
H-Ö:
H
Hydrolysis
Biodegradation
Photolysis
Precipitation-Dissolution
Adsorption-Desorption
Sedimentation
Bioconcentration
Reduction-Oxidation

FIGURE II-2 SPECIATION, TRANSPORT AND TRANSFORMATION PROCESSES IN THE AQUATIC ENVIRONMENT

other surface water body. The processes fall into four categories as follows:

- Loading Processes
  The rates at which waste discharges, atmospheric deposition, and land runoff introduce toxicants into natural waters influence resulting pollutant levels.

- Speciation Processes
  Acid-Base Equilibria - The pH of a natural water determines the fraction of an organic acid or base in neutral or ionic states, and therefore influences volatility.

  Sorption - Hydrophobic organic compounds sorb to suspended matter; their subsequent fate is influenced by the fate of the suspended matter.

- Transport Processes
  Precipitation-Dissolution - Solubility limits of both organic and inorganic pollutants can cause a pure pollutant phase to form restricting its availability to transport and transformation processes or substantially changing the transport route.

  Advection - Hydraulic flows transport pollutants which are dissolved or sorbed on suspended sediments into and out of particular aquatic habitats.

  Volatilization - Organic pollutants may enter the atmosphere from a water body, thereby reducing aquatic concentrations.

  Sedimentation - Deposition of suspended sediments containing sorbed pollutants, as well as direct sorption onto or desorption from bottom sediments can alter pollutant concentrations.

- Transformation Processes

  Biodegradation - Microbial organisms metabolize pollutants, altering their toxicity in the process.

  Photolysis - The absorption of sunlight by pollutants causes chemical reactions which affect their toxicity.

  Hydrolysis - The reaction of a compound with water frequently produces smaller, simpler organic products.

  Reduction-Oxidation - Reactions of organic pollutants and metals which involve the subtraction or addition of electrons strongly influence their environmental properties. For organics, nearly all significant redox reactions are microbially mediated.

- Bioaccumulation

  Bioconcentration - Uptake of toxic pollutants into biota via passive means, e.g. absorption through fish gills.

  Biomagnification - Uptake of toxicants into biota via consumption of contaminated food.

Once the pertinent processes have been identified, the physical compartments of the environment between which the transport processes act must be delineated. For most water bodies, compartments representing the atmosphere, bottom sediments, and one or more water elements are sufficient. These methods are capable of representing transport of pollutants between the atmosphere and a water body. But rather than calculating atmospheric concentrations of a pollutant, these methods generally assume them to be close to zero unless available data indicate otherwise. Bottom sediments, however, frequently accumulate high levels of organic pollutants. Because of the difficulty of modeling the behavior of toxicants in sediments, usually assumptions which approximate only the removal or addition of a pollutant to the water column are made. These approximations are presented in the individual chapters on each water body.

The next step in assessing the aquatic fate of toxic pollutants is to represent the advection or flow of water. Figure II-3 illustrates a representation of rivers as a segregated flow system and lake layers as completely mixed flow systems. Although these models are simple, they serve as adequate first-approximations of real systems. Refinements and limitations of these flow system models are considered in the individual chapters on rivers, lakes, and estuaries.

The transport and transformation processes responsible for the removal of a pollutant from the water column are considered next. First-order rate expressions adequately represent all of the processes considered here. The first-order decay of a pollutant by a process is represented as follows:

$$\text{Rate of Pollutant Removal} = k_i \cdot C_T \qquad \text{(II-3)}$$

where

k_i = first-order rate constant for process i
C_T = total concentration of pollutant

The rate constant for a process is specific to both the chemical it acts upon and the local environment in which it acts.

When all the first-order processes act independently, the total rate of pollutant removal is:

$$\text{Total Rate of Removal} = k_T \cdot C_T \qquad \text{(II-4)}$$

where

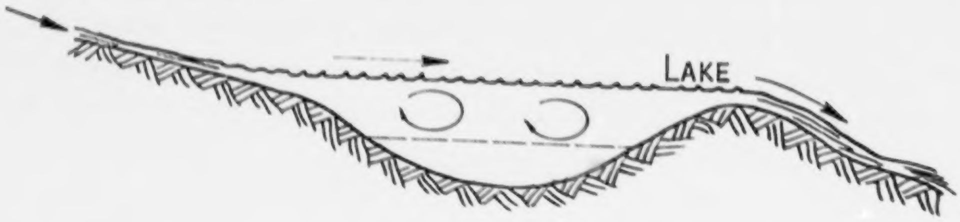
$$k_T = k_{vm} + k_S + k_B + k_P + k_H \qquad \text{(II-5)}$$

k_{vm} = specific mixed-body volatilization rate constant

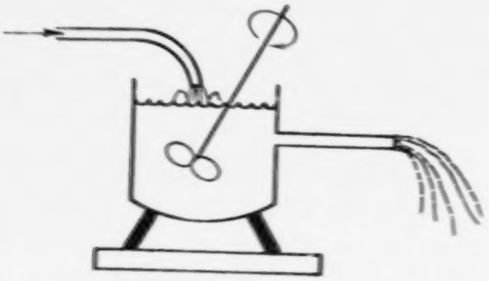
k_S = specific rate constant for removal to bottom sediment

COMPLETELY MIXED FLOW

NATURAL SYSTEM:



IDEALIZATION:



SEGREGATED FLOW

NATURAL SYSTEM:

IDEALIZATIONS:

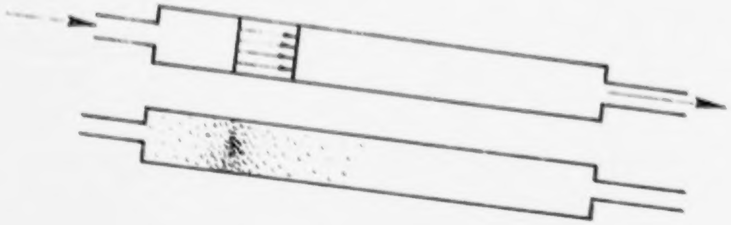

PLUG FLOW
FLOW WITH AXIAL DISPERSION

FIGURE II-3 FLOW SYSTEM REPRESENTATIONS

k_B = specific rate constant for biodegradation

k_P = specific rate constant for photolysis

k_H = specific rate constant for hydrolysis

The additivity of processes which are first-order with respect to pollutant concentration is particularly convenient for analysis.

Many of the decay processes are influenced by the chemical state of the toxicant. For example, sorbed pollutants cannot volatilize. Mathematical representations of equilibria between two species of a chemical can be reduced to the following type of equation. This type of equation serves well at the low solute concentrations encountered in waste waters and natural waters:

$$C_i = K_{ij} C_j \tag{II-6}$$

where

C_i = concentration of form i

K_{ij} = equilibrium constant

C_j = concentration of form j

It is also convenient to know the fraction of the total pollutant concentration which is in a given state:

$$\alpha_i = \frac{C_i}{C_T} \tag{II-7}$$

where

C_i = concentration in state i

$C_T = C + C_S$

C = total dissolved phase pollutant concentration

C_S = total sorbed phase pollutant concentration

To complete the assessment of the aquatic fate of a pollutant the mode of entry into the aquatic environment must be considered. Many pollutants enter in dissolved or sorbed form from a point source. In this case, a simple mixing computation is sufficient to determine the initial concentration of a pollutant in the water body. Other cases include spills, non-point sources, and desorption from sediments. Chapter 4 presents methods for dealing with these cases.

The user may now reckon the concentration of a pollutant in a given water body. The equations which yield the desired results are specific to each surface water type and are developed in the individual chapters on lakes, rivers, and estuaries. An equation representative of those in each chapter is presented in Table II-10. The individual chapters go into greater detail about factors influencing rate processes and interactions with other important phenomena in each water body (See Sections 4.9, 5.6, 6.4.3, and 6.4.5).

2.2.2 Use of Assessment Techniques as Screening Tools

2.2.2.1 Making Conservative Assumptions

With the computational methods presented in this document, the user could produce a relatively complete analysis of the aquatic fate of a pollutant. The goal of this screening method, however, is to determine--with a minimum of effort--whether toxicants are likely to reach problem levels in surface water bodies for either existing or projected loading rates. The user can minimize the effort expended in screening a pollutant by starting with a simple approach which incorporates conservative assumptions about the fate of a pollutant. Conservative assumptions are designed to yield higher calculated environmental concentrations than

TABLE II-10

EXPRESSIONS FOR TOXIC POLLUTANT LEVELS
IN VARIOUS WATER BODIES

Water Body	Expression for Steady-State Pollutant Concentration
Rivers (Chapter IV)	$C = C_o \exp\left[\frac{-k'_v - \sum K_i}{1 + K_p S} \cdot \frac{X}{U}\right]$ (IV-115) where x = distance downstream U = river velocity C = total dissolved phase concentration
Impoundments (Chapter V)	$C = C_{in}/(1 + T_w \times k)$ (V-47) where T_w = hydraulic residence time C = total dissolved and sediment phase concentration
Estuaries	$C_i = C_{i=1} \frac{f_i}{f_{i-1}} B_i$ (VI-33) $B_i = \frac{r_i}{1 - (1-r_i)e^{-kt}}$ (VI-34) where C_i = concentration in segment i f_i = fraction of fresh water in segment i r_i = segment i exchange ratio t = time expressed in tidal cycles

probably exists in the real system. If these higher concentrations are below the water quality criterion under consideration, a violation of the standard is unlikely. If the initial predictions are higher than the standard, the user may successively refine the approach until it becomes apparent that either the standard will be met or that a more detailed study is necessary.

Three levels of refinement in assessing the aquatic fate of a pollutant are considered here. In order of increasing complexity, they are:

1) Treating the pollutant as a conservative substance

2) Considering transport and speciation processes

3) Considering transformation, transport, and speciation processes.

Each approach has advantages and limitations which the user should consider. By following this sequence of refinements, the user should be able to eliminate cases where water quality problems are unlikely with a minimum of time and effort.

2.2.2.2 Treating the Pollutant as a Conservative Substance

The simplest approach to estimating the concentration of a toxic pollutant is to assume it behaves conservatively (i.e. does not undergo reaction):

$$k_T = 0$$

Unless an internal source of the pollutant exists, this approach will yield the highest possible pollutant levels since pollutant decay and removal processes are neglected. The obvious advantage of this approach is that it requires no chemical or environmental data to evaluate rate and equilibrium constants. The only data needed are pollutant loads and hydrological parameters. Its major drawback is that it neglects the possibility of a compound accumulating in another environmental compartment, especially bedded sediments. This could result in the underestimation of the duration of the exposure of an aquatic habitat to a chemical. Although the duration of exposure may be underestimated, water column concentrations would not exceed the upper limits predicted by this approach at any time during the exposure period. The fate of conservative pollutants in rivers, impoundments, and esturaries is discussed in Sections 4.1.9, 5.6.1, and 6.4.

2.2.2.3 Considering Transport and Speciation Processes

This refinement incorporates those processes which influence pollutant transport out of the aquatic environment but neglects those processes which chemically alter the compound. Transport processes strongly depend upon chemical speciation, which therefore must be included. The rate constant for first-order pollutant attenuation in this approach is:

$$k_T = k_S + k_{vm} \tag{II-8}$$

where

k_S = specific rate constant for removal to bottom sediment

k_{vm} = specific mixed body volatilization rate constant.

This approach requires more information on the properties of the toxicant and the environment than when the pollutant is assumed to behave conservatively, but the necessary data are much more readily available than that required to characterize transformation processes. Nearly all the chemical data necessary to characterize acid-base equilibria, sediment sorption, solubility limitations, and volatilization for the organitza priority pollutants are presented in tables in Sections 2.1.5, 2.3.1, and 2.4.2. The necessary environmental data can usually be obtained or estimated with a minimal amount of effort. Because of the demonstrated importance of transport processes and the relative simplicity of assessing them, this is a good intermediate step between the simplest and most complicated approaches.

Transport and speciation processes are applied specifically to rivers, impoundments, and estuaries in Sections 4.9, 5.6, 6.4.3, and 6.4.5.

2.2.2.4 Considering Transformation, Transport, and Speciation Processes

The most complex model which the user can employ using these screening methods includes consideration of transformation, transport, and speciation processes. With this approach, the rate constant for first-order attenuation of a pollutant is:

$$k_T = k_S + k_{vm} + k_B + k_P + k_H \qquad \text{(II-9)}$$

where

k_B = specific rate constant for biodegradation

k_P = specific rate constant for photolysis

k_H = specific rate constant for hydrolysis

The inclusion of the degradative processes (i.e. biodegradation, photolysis, and hydrolysis), considerably increases the chemical and environmental data required to model a compound's fate. Rather than accurately determining all the constants for speciation, transport, and transformation, the user should first ascertain which processes are the most significant for a compound. As a first step the user should obtain data on the properties of the chemical which influence its aquatic fate from this document or other sources. From compound specific data, it is usually possible to eliminate some processes from consideration. For organic priority pollutants, consulting the ratings of the relative importance of aquatic processes for the fate of each compound, Table II-11, may aid the user in eliminating unimportant processes. Once the most significant processes have been identified, the user should collect the environmental data necessary to determine site specific constants. These site specific constants are then applied in the appropriate equation for each water body type to obtain the best estimate of the actual pollutant concentrations in

TABLE II-11

RELATIVE IMPORTANCE OF PROCESSES INFLUENCING AQUATIC FATE OF ORGANIC PRIORITY POLLUTANTS (After Callahan *et al.*, 1979)

Compound	Process					
	Sorption	Volatilization	Biodegradation	Photolysis-Direct	Hydrolysis	Bioaccumulation
PESTICIDES						
Acrolein	-	+	+	+	-	-
Aldrin	+	+	?	-	-	+
Chlordane	+	+	?	-	-	+
DDD	+	+	-	-	-	+
DDE	+	+	-	+	-	+
DDT	+	+	-	-	+	+
Dieldrin	+	+	-	+	-	+
Endosulfan and Endosulfan Sulfate	+	+	+	?	+	-
Endrin and Endrin Aldehyde	?	?	?	+	-	+
Heptachlor	+	+	-	?	++	+
Heptachlor Epoxide	+	-	?	?	-	+
Hexachlorocyclohexane (α,β,δ isomers)	+	?	+	-	-	-
-Hexachlorocyclohexane (Lindane)	+	-	+	-	-	-
Isophorone	-	-	?	+	-	-
TCDD	+	-	-	?	-	+
Toxaphene	+	+	+	-	-	+
PCBs and RELATED COMPOUNDS						
Polychlorinated Biphenyls	+	+	+[a]	?	-	+
2-Chloronaphthalene	-	?	+	+	-	-
HALOGENATED ALIPHATIC HYDROCARBONS						
Chloromethane (methyl chloride)	-	+	-	-	-	-
Dichloromethane (methylene chloride)	-	+	?	-	-	-
Trichloromethane (chloroform)	-	+	?	-	-	-
Tetrachloromethane (carbon tetrachloride)	?	+	-	-	-	?
Chloroethane (ethyl chloride)	-	+	?	-	+	-
1,1-Dichloroethane (ethylidene chloride)	-	+	?	-	-	-
1,2-Dichloroethane (ethylene dichloride)	-	+	?	-	-	-
1,1,1-Trichloroethane (methyl chloroform)	-	+	-	-	-	-
1,1,2-Trichloroethane	?	+	-	-	-	?
1,1,2,2-Tetrachloroethane	?	+	-	-	-	?

Key to Symbols:

++ Predominant fate determining process	- Not likely to be an important process
+ Could be an important fate process	? Importance of process uncertain or not known

TABLE II-11 (continued)

Compound	Process					
	Sorption	Volatilization	Biodegradation	Photolysis-Direct	Hydrolysis	Bioaccumulation
Hexachloroethane	?	?	?	?	?	+
Chloroethene (vinyl chloride)	+	-	-	-	-	-
1,1-Dichloroethene (vinylidene chloride)	?	+	?	-	-	?
1,2-*trans*-Dichloroethene	-	+	?	-	-	-
Trichloroethene	-	+	?	-	-	-
Tetrachloroethene (perchloroethylene)	-	+	+	-	-	-
1,2-Dichloropropane	?	+	-	?	+	?
1,3-Dichloropropene	?	+	-	?	+	-
Hexachlorobutadiene	+	+	?	-	?	+
Hexachlorocyclopentadiene	+	+	-	+	+	+
Bromomethane (methyl bromide)	-	+	-	-	+	-
Bromodichloromethane	?	?	?	?	-	+
Dibromochloromethane	?	+	?	?	-	+
Tribromomethane (bromoform)	?	+	?	?	-	+
Dichlorodifluoromethane	?	+	-	?	-	?
Trichlorofluoromethane	?	+	-	-	-	?
HALOGENATED ETHERS						
Bis(choromethyl) ether	-	-	?	-	++	-
Bis(2-chloroethyl) ether	-	+	-	-	-	?
Bis(2-chloroisopropyl) ether	-	+	-	-	-	?
2-Chloroethyl vinyl ether	-	+	?	-	+	-
4-Chlorophenyl phenyl ether	+	?	?	+	-	+
4-Bromophenyl phenyl ether	+	?	?	+	-	+
Bis(2-chloroethoxy) methane	-	-	?	-	+	?
MONOCYCLIC AROMATICS						
Benzene	+	+	-	-	-	-
Chlorobenzene	+	+	-	?	-	+
1,2-Dichlorobenzene (*o*-dichlorobenzene)	+	+	-	?	-	+
1,3-Dichlorobenzene (*m*-dichlorobenzene)	+	+	?	?	?	+
1,4-Dichlorobenzene (*p*-dichlorobenzene)	+	+	-	?	-	+
1,2,4-Trichlorobenzene	+	+	-	?	-	+
Hexachlorobenzene	+	-	-	-	-	-

Key to Symbols:

++ Predominant fate determining process
+ Could be an important fate process
- Not likely to be an important process
? Importance of process uncertain or not known

TABLE II-11 (continued)

Compound	Process					
	Sorption	Volatilization	Biodegradation	Photolysis-Direct	Hydrolysis	Bioaccumulation
Ethylbenzene	?	+	?	-	-	-
Nitrobenzene	+	-	-	+	-	-
Toluene	+	+	?	-	-	-
2,4-Dinitrotoluene	+	-	-	+	-	?
2,6-Dinitrotoluene	+	-	-	+	?	?
Phenol	-	+	+	+	-	-
2-Chlorophenol	-	-	?	+	-	-
2,4-Dichlorophenol	-	-	++	-	-	-
2,4,6-Trichlorophenol	?	-	?	?	-	-
Pentachlorophenol	+	-	+	+	-	+
2-Nitrophenol	-	-	-	++[b]	-	-
4-Nitrophenol	+	-	-	++	-	-
2,4-Dinitrophenol	+	-	-	++[b]	-	-
2,4-Dimethyl phenol (2,4-xylenol)	-	-	?	+	-	-
p-chloro-*m*-cresol	-	-	?	++	-	-
4,6-Dinitro-*o*-cresol	+	-	-	++	?	?
PHTHALATE ESTERS						
Dimethyl phthalate	+	-	+	-	-	+
Diethyl phthalate	+	-	+	-	-	+
Di-n-butyl phthalate	+	-	+	-	-	+
Di-n-octyl phthalate	+	-	+	-	-	+
Bis(2-ethylhexyl) phthalate	+	-	+	-	-	+
Butyl benzyl phthalate	+	-	+	-	-	+
POLYCYCLIC AROMATIC HYDROCARBONS						
Acenaphthene[c]	+	-	+	+	-	-
Acenaphthylene[c]	+	-	+	+	-	-
Fluorene[c]	+	-	+	+	-	-
Naphthalene	+	-	+	+	-	-
Anthracene	+	+	+	+	-	-
Fluoranthene[c]	+	+	+	+	-	-
Phenanthrene[c]	+	+	+	+	-	-
Benzo(a)anthracene	+	+	+	+	-	-
Benzo(b)fluoranthene[c]	+	-	+	+	-	-
Benzo(k)fluoranthene[c]	+	-	+	+	-	-
Chrysene[c]	+	-	+	+	-	-

Key to Symbols:

++ Predominant fate determining process	- Not likely to be an important process
+ Could be an important fate process	? Importance of process uncertain or not known

TABLE II-11 (continued)

Compound	Process					
	Sorption	Volatilization	Biodegradation	Photolysis-Direct	Hydrolysis	Bioaccumulation
Pyrene[c]	+	-	+	+	-	-
Benzo(ghi)perylene[c]	+	-	+	+	-	-
Benzo(a)pyrene	+	+	+	+	-	-
Dibenzo(a,h)anthracene[c]	+	-	+	+	-	-
Indeno(1,2,3-cd)pyrene[c]	+	-	+	+	-	-
NITROSAMINES AND MISC. COMPOUNDS						
Dimethylnitrosamine	-	-	-	++	-	-
Diphenylnitrosamine	+	-	?	+	-	?
Di-n-propyl nitrosamine	-	-	-	++	-	-
Benzidine	+	-	?	+	-	-
3,3'-Dichlorobenzidine	++	-	-	+	-	-
1,2-Diphenylhydrazine (Hydrazobenzene)	+	-	?	+	-	+
Acrylonitrile	-	+	?	-	-	+

Key to Symbols:

++ Predominate fate determining process	- Not likely to be an important process
+ Could be an important fate process	? Importance of process uncertain or not known

Notes

[a] Biodegradation is the only process known to transform polychlorinated biphenyls under environmental conditions, and only the lighter compounds are measurably biodegraded. There is experimental evidence that the heavier polychlorinated biphenyls (five chlorine atoms or more per molecule) can be photolyzed by ultraviolet light, but there are no data to indicate that this process is operative in the environment.

[b] based on information for 4-nitrophenol

[c] Based on information for PAH's as a group. Little or no information for these compounds exists.

the environment that these methods are capable of making. (See Sections 4.9, 5.6, 6.4.3, and 6.4.5).

Frequently, kinetic and equilibrium constants will depend on the values of parameters which the user must estimate (e.g. pH). In such cases, assuming conservative values is the best policy. However, calculations using a range of values may identify processes for which a more careful determination of the key environmental and chemical parameters is warranted.

Example II-1 is an overall example for this chapter. It demonstrates the initial steps a user would take in applying these methods to assess the fate of a particular organic pollutant. The example follows the three level analysis described above and also draws upon some of the procedures for specific environmental processes which are developed later in this chapter. This example can serve as a guide to evaluating the importance of the various fate influencing processes for a particular pollutant.

EXAMPLE II-1

Pentachlorophenol in the Aurum Mirth Watershed

Pentachlorophenol enters the Aurum Mirth River from a continuous point source. The river is the sole tributary to Lake Castile. After mixing at the point of entry, the concentration of pentachlorophenol in the river is 20 μg/l. The travel time from the point of contamination with pentachlorophenol to Lake Castile is about 6 days. The mean hydraulic residence time in Lake Castile is 10 days.

Use the screening methods to determine which chemical and environmental parameters are of the greatest importance for predicting the fate of pentachlorophenol in the watershed's surface waters.

1) TREATING PENTACHLOROPHENOL AS A CONSERVATIVE SUBSTANCE

The first step in the screening method is to assess the fate of pentachlorophenol treating it as a conservative substance. Sections 4.1.9, 5.6.1, and 6.4 discuss the fate of conservative pollutants in rivers, lakes, and estuaries. In this case, we assume no further dilution of the pentachlorophenol occurs in either the lake or the river. Consequently, the conservative pollutant approach predicts a mean concentration in the river and lake of 20 μg/l.

Table II-2 lists a proposed water quality standard for pentachlorophenol. The 24 hour mean concentration must be less than 6.2 μg/l. Since 20 μg/l, exceeds this standard, a second level assessment is in order.

Prior to applying the next two levels of analysis it is worthwhile to check Table II-11 for the relative importance of the different transformation and transport processes. Table II-11 summarizes the influence of the aquatic processes on pentachlorophenol as follows:

- Sorption - Important process
- Volatilization - Not an important process
- Biodegradation - Important process
- Direct Photolysis - Important process
- Hydrolysis - Not an important process
- Bioaccumulation - Important process

It will be instructive to compare these statements to the results of the screening methodology.

2) CONSIDERING TRANSPORT AND SPECIATION PROCESSES

To analyze transport and speciation processes, first examine each process for its potential influence on the fate of pentachlorophenol.

Speciation Processes

Acid-Base Effects (Section 2.3.1)

The chemical and environmental parameter governing acid-base effects are:

Chemical Parameters:

- pK_a or pK_b - acid or base equilibrium constants

Environmental Parameters:

- pH - hydrogen ion concentrations

The pK_a of pentachlorophenol is 4.74, as shown in Table II-13. According to Table II-12, at least 90 percent of the pentachlorophenol will be in the anionic state at pH's greater than 5.74. As long as the pH in the Aurum Mirth River and Lake Castile remain above 5.74, the properties of pentachlorophenol as measured for neutral waters will remain unaffected. But, because pH's below 5.74 could significantly alter the behavior of the compound, it is important to determine actual surface water pH values.

Sorption (Section 2.3.2)

The key environmental and chemical parameters which influence sorption are:

Chemical parameters:

- K_{ow} - octanol-water coefficient
- S_w - solubility in water

Environmental Properties:

- Suspended sediment concentration
- organic carbon content of the suspended sediment

Table II-8 lists the solubility and octanol-water coefficient of pentachlorophenol as:

$$S = 14 \text{ mg/l}$$
$$K_{ow} = 10^5$$

Assuming an organic carbon content of 2 percent for the suspended sediments, calculate K_p using Equations II-18 and II-16:

$$K_p = (.02)\ (.63)\ (10^5) = 1300$$

According to Table II-14, greater than 10 percent of the pentachlorophenol will be in the sorbed state at suspended sediment concentrations exceeding 100 mg/l. The relatively strong sorption of pentachlorophenol dictates that the suspended sediment concentration in the Aurum Mirth River and the sediment trapping efficiency of Lake Castile be investigated further. Sorption of pentachlorophenol potentially affects both its speciation and its transport rates.

Transport Processes

Solubility Limitations (Section 2.4.1)

The most important chemical and environmental factors which influence solubility of a compound are:

Chemical Parameters:

- S_w - Aqueous equilibrium solubility

Environmental Parameters:

- T - Temperature
- Salinity

Table II-8 lists the solubility limit for pentachlorophenol as 14 mg/l (14000 µg/l). At no point in the Aurum Mirth watershed should the solubility of pentachlorophenol restrict the ability of the aqueous phase to transport it.

Volatilization (Section 2.4.2)

The most significant chemical and environmental properties which influence volatilization are:

Chemical Parameters:

- K_H - Henry's Law Contant

Environmental Parameters:

- k_a - reaeration constant

- V - wind speed

- Z - mixed depth of water body

It is possible to estimate the Henry's law constant for pentachlorophenol from its vapor pressure and aqueous solubility using Equation II-32. However, it is simpler to rule out volatilization as a significant transport process on the basis of the volatilization half-life of 100 days given in Table II-8. Because laboratory volatilization half-lives are shorter than the true environmental values, it is safe to assume the environmental half-life will be much greater than 100 days. Given a total system mean hydraulic residence time of only 16 days (6+10), volatilization can be safely neglected.

Summary. Acid-base equilibria and sorption significantly influence the transport and speciation of pentachlorophenol in the aquatic environment. Acid-base effects do not influence the near-neutral volatilization and photolysis rate constants presented in this document as long as pH's remain above 5.7. Sorption is a potentially important speciation process. Consequently, the pH values and suspended sediment concentrations should be determined in order to accurately evaluate these processes.

The strong tendency of pentachlorophenol to sorb on sediments may result in sedimentation serving as a significant removal process in Lake Castile. The absence of net sediment deposition in the river implies that transport processes do not reduce pentachlorophenol concentrations in the Aurum Mirth. Thus, the second level analysis predicts a total concentration of 20 $\mu g/l$ of pentachlorophenol in the Aurum Mirth River with lower levels possible in the lake. Because the predicted river concentrations exceed the standard, the third level model is necessary.

3) CONSIDERING TRANSFORMATION, TRANSPORT, AND SPECIATION PROCESSES

To consider transformation, transport, and speciation processes, the transformation processes which were neglected in the level two analysis must be examined for their potential importance in influencing the rate of pentachlorophenol degradation.

Transformation Processes

Biodegradation (Section 2.5.1)

The key chemical and environmental variables which influence biodegradation are:

Chemical Parameters:

- Metabolic Pathway (growth or co-metabolism)
- k_B - Biodegradation rate constant

Environmental Parameters:

- Bacterial population size
- State of adaptation
- Inorganic nutrient concentrations - Phosphorus
- Dissolved oxygen
- Temperature
- Pollutant concentration

According to Table II-23, pentachlorophenol is potentially biodegradable, although adaptation may be slow. The reported specific rate constant values, 0.1 to 1.0 per day, in Table II-24 are in the same range as the 0.05 to 0.5 per day values suggested in Table II-23. Although both rate constants were determined under laboratory rather than environmental conditions, they do indicate that pentachlorophenol can degrade very rapidly.

Table II-24 also indicates that pentachlorophenol is used by bacteria as a growth substrate. Thus, the time required for adaptation is of primary concern. The most important environmental factors for determining whether microorganisms in the Aurum Mirth watershed will adapt to degrade pentachlorophenol are previous exposure, time, and the actual concentrations of pentachlorophenol in the surface waters (too low--no enzyme induction; too high--may have toxic effect on microbiota).

Photolysis (Section 2.5.2)

The key chemical and environmental characteristics influencing the rate of photolysis are:

Chemical Properties

- k_{do} - Near-surface rate constant

or

- $\varepsilon(\lambda)$ - Light absorption coefficient of pollutant, and
- ϕ - Quantum yield

Environmental Properties:

- I - Solar radiant flux

- Z - Mixed depth of water body

- K - Diffuse light attenuation coefficient

  a) Z_{sd} - Secchi disc depth

  b) C_{ss} - Suspended sediment concentration

  C_{DOC} - Dissolved organic carbon concentration

  C_a - Chlorophyll pigment concentration

According to Table II-29, the near-surface photolysis rate constant for pentachlorophenol is .46/day. The size of the rate constant implies that photolysis would be an important factor if the water bodies are not too deep or too turbid. Thus, it is important to gather information on the water depths, and to estimate the light attenuation coefficients, and the solar radiant flux in the Aurum Mirth watershed.

Hydrolysis (Section 2.5.3)

The important parameters influencing the rate of hydrolysis are:

Chemical Parameters:

- k_a, k_n, k_b - Acid, neutral, and base catalyzed hydrolysis rate constants

Environmental Properties:

- pH - concentration of hydrogen ion in the water bodies.

Table II-31 gives acid and base hydrolysis rate constants for pentachlorophenol of 1.1×10^{4} and 3.3 liter mole^{-1} day^{-1}. The neutral rate constant is 5.8×10^{-3} per day. The same table lists a half life of 100 days at pH = 7. Because the acid catalyzed rate constant is large, significantly higher rates could occur at lower pH's. Using Equation II-85, the rate constant for pH = 5 is:

$$k_H = 1.1 \times 10^{4} (10^{-5}) + 5.8 \times 10^{-3} + 3.3 (10^{-9})$$

$$= .23 \text{ day}^{-1}$$

At this lower pH, degradation by abiotic hydrolysis would be very rapid. Thus, determining the pH in the Aurum Mirth River and Lake Castile is very important.

Summary

The consideration given to transformation, transport, and speciation processes indicates the following processes are of potential importance to the fate of pentachlorophenol in the Aurum Mirth watershed:

- Acid-Base Effects
- Sorption
- Biodegradation
- Photolysis
- Hydrolysis

Since the three transformation processes are potentially important, there is a good possibility that the initial pentachlorophenol concentration of 20 μg/l will be reduced below the 6.2 μg/l standard. Therefore further analysis as presented in the specific water body sections is warranted.

The results of this example agree with the summary of rate processes given in Table II-11 except for the case of hydrolysis. This demonstrates that the process summary table can serve as a useful guide but should be supplemented with actual data whenever possible.

END OF EXAMPLE II-1

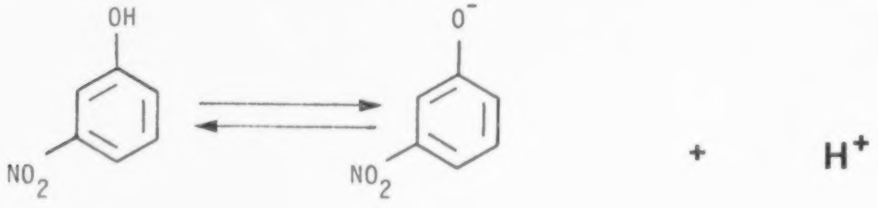
2.3 SPECIATION PROCESSES

2.3.1 Acid-Base Effects

The fate of toxic organics which are either acids or bases can be strongly affected by the concentration of hydrogen ions in a water body. It is therefore necessary to have a means for estimating this influence. This section will first present a brief review of acid-base equilibria and then will give a technique for quantifying the influence of hydrogen ion concentration on the behavior of toxicants.

2.3.1.1 Acid-Base Equilibria

Acids by definition donate hydrogen ions, H^+, to solution. Bases, by definition, accept hydrogen ions from solution. 2-Nitrophenol, one of the 129 priority pollutants, is an acid and donates hydrogen ions as shown by the following reaction:



2-nitrophenol — 2-nitrophenolate + hydrogen ion

(HP) — **(P^-)** — **(H^+)**

Acid-base reactions are extremely fast and can be represented by equilibrium expressions. For the above reaction the expression would be:

$$\frac{[H^+]\,[P^-]}{[HP]} = K_a \qquad \text{(II-10)}$$

where

$[H^+]$ = concentration of hydrogen ions, moles/liter

$[P^-]$ = concentration of nitrophenolate ions, moles/liter

$[HP]$ = concentration of undissociated nitrophenol, moles/liter

K_a = an equilibrium constant for acid dissociation (also called an acidity constant)

The extent to which any acid will donate hydrogen ions to the solution depends on how many hydrogen ions are in solution (the concentration of hydrogen ions) and on the strength of the acid.

The concentration of free hydrogen ions in natural waters can range from about 10^{-4} to 10^{-10} moles per liter. Hydrogen ion concentrations are normally expressed in pH units. In dilute solutions, such as natural waters, pH is defined as the negative logarithm of the molar hydrogen ion concentration ($pH = -\log_{10} [H^+]$). For the above two concentrations the pH values are 4 and 10.

The strength of an acid is quantified by the equilibrium constant, K_a. For very strong acids (those which most readily donate hydrogen ions) the value of this constant is greater than unity. Included in this group are strong acids such as hydrochloric and nitric acid. Toxic organic acids, though, are generally weak acids and have K_a values between 10^{-3} and 10^{-9}. K_a values are typically expressed in terms of negative base ten logarithms. When this approach is used the equilibrium constants are called "pK_a" ($pK_a = -\log_{10} K_a$).

When the pH of a solution is the same as the pK_a value of an acid (i.e. $pH = pK_a$), 50 percent of the acid will have donated its hydrogen ions to the solution and will exist as a charged anionic species. For pH values greater than the pK_a value by one or more units, the acid will have donated essentially all of its hydrogen ions to the solution and will exist in the anionic form (e.g. P^-).

The extent to which any base will extract hydrogen ions from solution depends upon the concentration of hydrogen ions in solution (pH) and on the strength of the base. The strength of a base is quantified by an equilibrium constant, K_b. For very strong bases (those that most readily extract hydrogen ions from solution) the value of K_b is of the order of 1. Toxic organic bases are generally weak and have K_b values between 10^{-3} and 10^{-10}. In a manner similar to acids, K_b is typically expressed in terms of negative base ten logarithms and is called "pK_b" ($pK_b = -\log_{10} K_b$).

Water itself can behave as a weak acid or a weak base:

$$H_2O \rightleftharpoons H^+ + OH^- \quad \text{(acidic behavior)}$$

$$H_2O + H^+ \rightleftharpoons H_3O+ \quad \text{(basic behavior)}$$

Note that $[H^+] \cdot [OH^-] = K_w$

where

$[OH^-]$ = the concentration of hydroxide ion, moles/l

$K_w \cong 10^{-14}$, at $20^\circ C$

$pK_w \cong 14$, at $20^\circ C$

When the pH of a solution equals the pK_b of a base, 50 percent of the base has accepted hydrogen ions and will exist as a charged cationic species. For pH values greater than one unit above the value of ($pK_w - pK_b$), essentially all of the base will exist in electrically neutral form (e.g. NH_3). For pH values less than the value of ($pK_w - pK_b$) by 1 or more units the base will essentially exist in the electrically charged cationic form (e.g. NH_4^+).

Table II-12 summarizes the behavior described above for acids and bases. Values for pK_a and pK_b for selected toxic organic acids and bases and values of pK_w are given in Table II-13.

TABLE II-12

OCCURRENCE OF ACIDS AND BASES IN NEUTRAL AND CHARGED FORMS AS A FUNCTION OF pH, pK_a, AND pK_b

Acids

Definition: Hydrogen ion donors

Example:

$HNO_3 \rightarrow H^+ + NO_3^-$

General Reaction:

$HP \rightarrow H^+ + P^-$

Speciation:

pH	Fraction in Neutral Form	Fraction in Ionic Form
pK_a+3	0.001	0.999
pK_a+2	0.01	0.99
pK_a+1	0.09	0.91
pK_a	0.5	0.5
pK_a-1	0.91	0.09
pK_a-2	0.99	0.01
pK_a-3	0.999	0.001

Bases

Definition: Hydrogen ion acceptors

Example:

$NH_3 + H^+ \rightarrow NH_4^+$

General Reaction:

$B + H^+ \rightarrow BH^+$

Speciation:

pH	Fraction in Neutral Form	Fraction in Ionic Form
pK_w-pK_b+3	0.999	0.001
pK_w-pK_b+2	0.99	0.01
pK_w-pK_b+1	0.91	0.09
pK_w-pK_b	0.5	0.5
pK_w-pK_b-1	0.09	0.91
pK_w-pK_b-2	0.01	0.99
pK_w-pK_b-3	0.001	0.999

TABLE II-13

pK_a AND pK_b VALUES FOR SELECTED TOXIC ORGANIC ACIDS AND BASES AND VALUES OF pK_w FOR WATER

Acids	pK_a [a]
Phenol	10.0
2-Chlorophenol	8.52
2,4-Dichlorophenol	7.85
2,4,6-Trichlorophenol	5.99
Pentachlorophenol	4.74
2-Nitrophenol	7.21
4-Nitrophenol	7.15
2,4-Dinitrophenol	4.09
2,4-Dimethylphenol	10.6
4,6-Dinitro-*o*-cresol	4.35
Bases	pK_b [b]
Benzidine	9.34, 10.43
Water	pK_w [c]
Freshwater	14.63 at 5°C
	14.53 at 10°C
	14.35 at 15°C
	14.17 at 20°C
	14.00 at 25°C
	13.82 at 30°C
Seawater	14.03 at 5°C
	13.81 at 10°C
	13.60 at 15°C
	13.40 at 20°C
	13.20 at 25°C
	13.00 at 30°C

Notes:

[a] All pK_a values from Callahan *et al* (1979)

[b] All pK_b values from Weast and Astle (1980)

[c] pK_w values from Stumm and Morgan (1981) and from Dickson and Riley (1979)

Since toxic organics almost always exist in very low concentrations and are at best only weak acids or weak bases, they will have little influence, if any, on the pH values of the water. The hydrogen ion concentration of the water will, however, determine whether acids or bases exist in neutral or ionic forms.

Values of pH for natural waters can be obtained from the USGS, the U.S. EPA, and state and local agencies. Waters with low alkalinities (e.g. $\leq$ 50 mg/l as $CaCO_3$, or 1 milliequivalent/liter) are quite susceptible to changes in pH due to natural processes such as photosynthesis and respiration and even to relatively small additions of strong acid or base. Selection of representative pH values for such waters will require more data than for systems with higher alkalinities where less change in pH can be anticipated.

2.3.1.2 Quantifying the Influence of pH on Toxicant Volatilization

Only electrically neutral species are directly volatile. Volatilization rate expressions must therefore use as the concentration of toxicant only that fraction which is electrically neutral (non-ionic). The fraction of an acid or base which is in the non-ionic form can be determined by use of the expressions given below:

For organic acids:

$$\alpha_{Ao} = \frac{Ao}{A} = \frac{1}{1 + 10^{(pH - pK_A)}} \qquad \text{(II-11)}$$

For organic bases:

$$\alpha_{Bo} = \frac{Bo}{B} = \frac{1}{1 + 10^{(pK_W - pK_B - pH)}} \qquad \text{(II-12)}$$

where

α_{Ao} = the decimal fraction of the organic acid which is in the electrically neutral (non-ionic) form

α_{Bo} = the decimal fraction of the organic base which is in the electrically neutral (non-ionic) form

A = the total dissolved concentrations of the toxic organic acid (e.g. $HP+P^-$), also called the analytical concentration of A

B = the total dissolved concentration of the toxic organic base (e.g. $BH^+ + B$), also called the analytical concentration of B

The rate expressions then become in general form:

$$R = k_v \alpha_{A_o} A \qquad \text{(II-13a)}$$

and

$$R = k_v \alpha_{B_o} B \qquad \text{(II-13b)}$$

where

R = rate of volatilization

k_v = specific rate constants for volatilization

EXAMPLE II-2

2-nitrophenol has been detected in the Alehandra Estuary, which has a pH of 8, at concentrations of 20 μg/l (total dissolved form). Determine the volatilization flux on a per unit area basis. Assume the volatilization rate constant, k_v, is 2 cm/hr.

From Table II-13, the pK_a of 2-nitrophenol is 7.21. The fraction present in the electrically neutral (non-ionic) form is:

$$\alpha_{Ao} = \frac{1}{1 + 10^{(pH-pK_a)}}$$

$$= \frac{1}{1 + 10^{(8.0-7.2)}}$$

$$= 0.14$$

From Equation II-13 the volatilization flux is:

$$R_v = 2 \text{ cm/hr } (0.14) \left(\frac{20 \ \mu g}{l}\right) \left(\frac{1000 \ l}{m^3}\right) \left(\frac{1 \ m}{100 \ cm}\right) = 56 \ \mu g \ hr^{-1} m^{-2}$$

END OF EXAMPLE II-2

2.3.2 Sorption on Suspended Sediments

2.3.2.1 Introduction

Sorption refers to the accumulation of a chemical in the boundary region of a solid-liquid interface. Sorption occurs when the net sorbate-sorbent attraction overcomes the solute-solvent attraction, where solute and sorbate refer to the sorbing species in solution and sorbed at the interface, respectively.

Sorption of chemicals in the natural environment is significant because the fates of sorbates and solutes can be significantly different. Sorbates are transported along with sediments, and can be deposited in river or lake beds to remain indefinitely. Sorbates are in many ways protected from transformation processes which would otherwise affect the solute. For example:

- Microbial degradation rates can be reduced. Steen et al. (1978) performed tests which showed that sorption of toxicants to suspended sediments renders some compounds unavailable for biodegradation in the adsorbed state.

- Volatilization is diminished. Since volatilization of a chemical occurs from the dissolved phase, the sorbate is not directly available for volatilization. Rather, the sorbate first desorbs before it volatilizes. Example II-4 will show the significant influence of sorption on volatilization.

- Direct photolysis of pollutants adsorbed on suspended particles is inhibited in some cases. Further, suspended solids deposited on the bed of a river, lake, or estuary, receive very little radiation for photolytic reactions.

The net interaction between the surface of a solid and sorbate can result from a variety of forces, including coulombic attraction, Van der Waals forces, orientation energy, induction forces, hydrogen bonding, and chemical forces (Reinbold et al., 1979). In the case of many organic compounds, the solute-solvent interaction is often weak so that even a weak sorbate-sorbent attraction can result in sorption. This type of sorption is referred to as hydrophobic sorption because of the importance of the weak solute-solvent attraction. Hydrophobic sorption will be the topic of much of the following discussion, but it is preceded by brief discussions of equilibrium isotherms and sorption kinetics.

2.3.2.2 Adsorption Isotherms

Adsorption isotherms describe the relationship between the amount of chemical sorbed and the equilibrium solution concentration. The most commonly used isotherms are:

- Langmuir Adsorption Isotherm. This equation was originally developed to describe adsorption of a gas to a solid surface, but has been used to describe solid-liquid sorption.

- Freundlich Adsorption Isotherm. This empirical equation is based on surface-free energy and monolayer capacity.

- Linear Adsorption Isotherm. This equation assumes that there is a linear relationship between the concentrations of solute and sorbate at equilibrium. It is valid for dilute solutions.

Figure II-4 shows example comparisons between the three isotherms, and includes the equations which describe each isotherm. The quantity X is the amount of sorbed chemical per mass of sediment, and C_w is the amount of dissolved chemical per volume of solution. The remaining variables are unknown parameters required to define the relationship between X and C_w. The linear isotherm has one unknown parameter (K_p), while both the Freundlich and Langmuir isotherms have two unknown parameters (k_f,n and m,b, respectively).

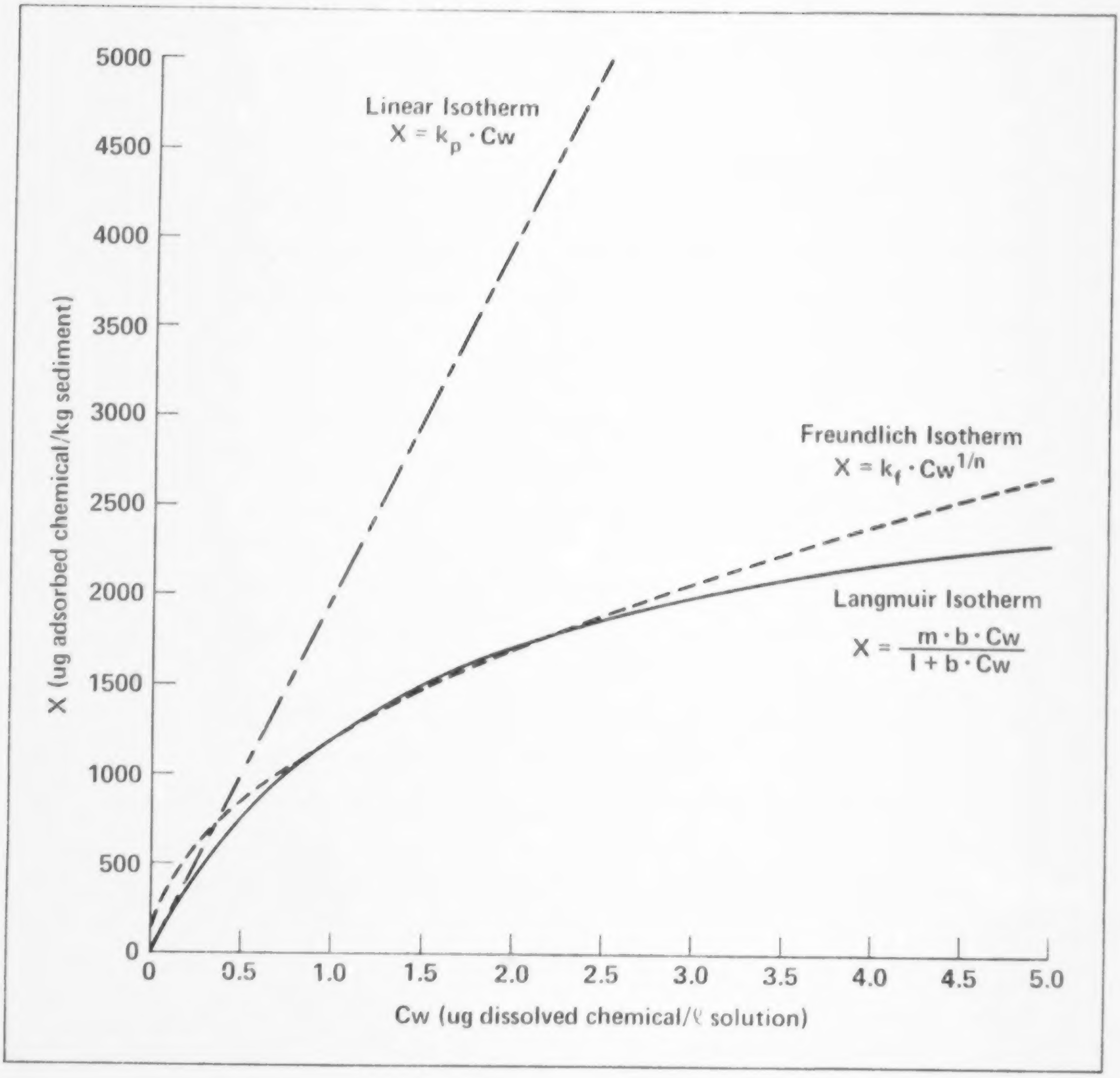


FIGURE II-4 ISOTHERMS FOR ADSORPTION OF A HYDROPHOBIC POLLUTANT ON SEDIMENTS

For the purposes of this document, analyses will mostly deal with dilute aqueous solution in the range where the linear isotherm is generally valid. This approach has the advantage of requiring that one unknown parameter (K_p) be evaluated, rather than two, and of being easier to manipulate mathematically. Section 2.3.2.4 will present methods of predicting the unknown parameter K_p.

2.3.2.3 Kinetics of Adsorption

Sorption of organic pollutants is often treated as a process which achieves rapid equilibrium so that expressions of kinetics are not needed. The equilibrium approach will be used in the remaining chapters of this document. However, a brief introduction will be given of sorption kinetics.

Studies of sorption kinetics are apparently few, with the result that parameters required in rate expressions are ill defined and applicable only under a specific set of conditions. Under these constraints, kinetics expressions become less attractive unless the user can determine values of the rate constants which apply to the specific system being investigated.

Most typically, kinetics expressions for sorption and desorption are chosen to be first order. Specifically,

$$\frac{\partial C_w}{\partial t} = -k_{sd}\left(C_w - \frac{X}{K_p}\right) \qquad \text{(II-14)}$$

expresses the kinetic expression for the solute and

$$\frac{\partial X}{\partial t} = -k_{sd}(X - K_p C_w) \qquad \text{(II-15)}$$

for the sorbate. The concentrations X and C_w are not necessarily equilibrium concentrations. In these two equations, the rate parameter k_{sd} is assumed to be the same whether adsorption or desorption is occurring. However, different rates could be used for each process.

Karickhoff (1979) investigated the sorption and desorption of organic pollutants and found that a very rapid component of adsorption preceded a much slower component of adsorption, and that first order kinetics were obeyed during each of the two periods. For the fast process, the time constant was found to range from 4 to 30 per hour, while for the slow process the time constant ranged from 0.06 to 1.5 per hour. Approximately half of the sorptive equilibrium was realized within minutes, while the slower component required days or weeks to complete. The slower second period was visualized as diffusive transfer to sorption sites that were inaccessible directly to the bulk water. Thus, equilibrium conditions are more likely to be rapidly attained when the number of easily accessible surface sites exceeds the amount of available sorbate, e.g. when suspended sediment concentrations are high.

2.3.2.4 Partition Coefficients for Organic Chemicals Obeying Linear Isotherms

The single unknown parameter, K_p, which relates the sorbate and solute for linear isotherms is called the partition coefficient. A number of studies have been completed which develop empirical relationships for partition coefficients in natural sediments. Several of these studies will be summarized here. Theoretically based methods of estimating partition coefficients exist, such as a thermodynamic approach described in Pavlou (1979); however, these will not be discussed here.

Karickhoff *et al*. (1979) examined the sorption of aromatic hydrocarbons and chlorinated hydrocarbons on natural sediments. They found it convenient to relate the partition coefficient directly to organic carbon content of the sediments as follows:

$$K_p = K_{oc} x_{oc} \qquad \text{(II-16)}$$

where

K_{oc} = partition coefficient expressed on an organic carbon basis

x_{oc} = mass fraction of organic carbon in sediment.

These workers were able to expand this relationship to segregate the influence of particle size as follows:

$$K_p = K_{oc}[0.2(1-f)x^s_{oc} + fx^f_{oc}] \qquad \text{(II-17)}$$

where

f = mass fraction of fine sediments ($d < 50\,\mu m$)

x^s_{oc} = organic carbon content of coarse sediment fraction

x^f_{oc} = organic carbon content of fine sediment fraction.

Karickhoff et al. (1979) were able to relate K_{oc} to the octanol-water partition coefficient and to the water solubility by the following relationships:

$$K_{oc} = 0.63\ K_{ow} \qquad \text{(II-18)}$$

where

K_{ow} = octanol-water partition coefficient (concentration of chemical in octanol divided by concentration of chemical in water, at equilibrium)

and

$$K_{oc} = -0.54 \log S_w + 0.44 \qquad \text{(II-19)}$$

where

S_w = water solubility of sorbate, expressed as a mole fraction.

The water solubilities of the compounds examined ranged from 1 ppb to 1000 ppm.

Hassett *et al*. (1980) found a similar relationship between K_{oc} and K_{ow} for organic energy-related pollutants. Figure II-5 shows the relationship. Data from Karickhoff *et al*. are included in the plot for comparison.

Prior to the work of Karickhoff *et al*., Chiou *et al*. (1977) investigated the relationship between octanol-water partitioning and aqueous solubilities for a wide variety of chemicals including aliphatic and aromatic hydrocarbons, aromatic acids, organochlorine and organophosphate pesticides, and polychlorinated biphenyls. Their results, shown in Figure II-6, cover more than eight orders of magnitude in solubility and six orders of magnitude in the octanol-water partition coefficient. The regression equation based on this figure is:

$$\log K_{ow} = 5.00 - 0.670 \log S_w \qquad \text{(II-20)}$$

where

S_w = solubility, in μmol/l

Brown and Flagg (1981) have extended the work of Karickhoff *et al*. by developing an empirical relationship between K_{ow} and K_{oc} for nine chloro-s-triazine and dinitroaniline compounds. They plotted their results, along with those of Karickhoff *et al*, as shown in Figure II-7. The combined data set produces the following correlation:

$$\log K_{oc} = 0.937 \log K_{ow} - 0.006 \qquad \text{(II-21)}$$

The linear correlation between K_{oc} and K_{ow} for the compounds studied by Brown and Flagg has a larger factor of uncertainty than those studied by Karickhoff *et al*.

The previous paragraphs have shown how the partition coefficient K_p can be predicted for organic hydrophobic compounds which obey a linear isotherm relationship. First, K_{oc} is predicted based on either water solubility or

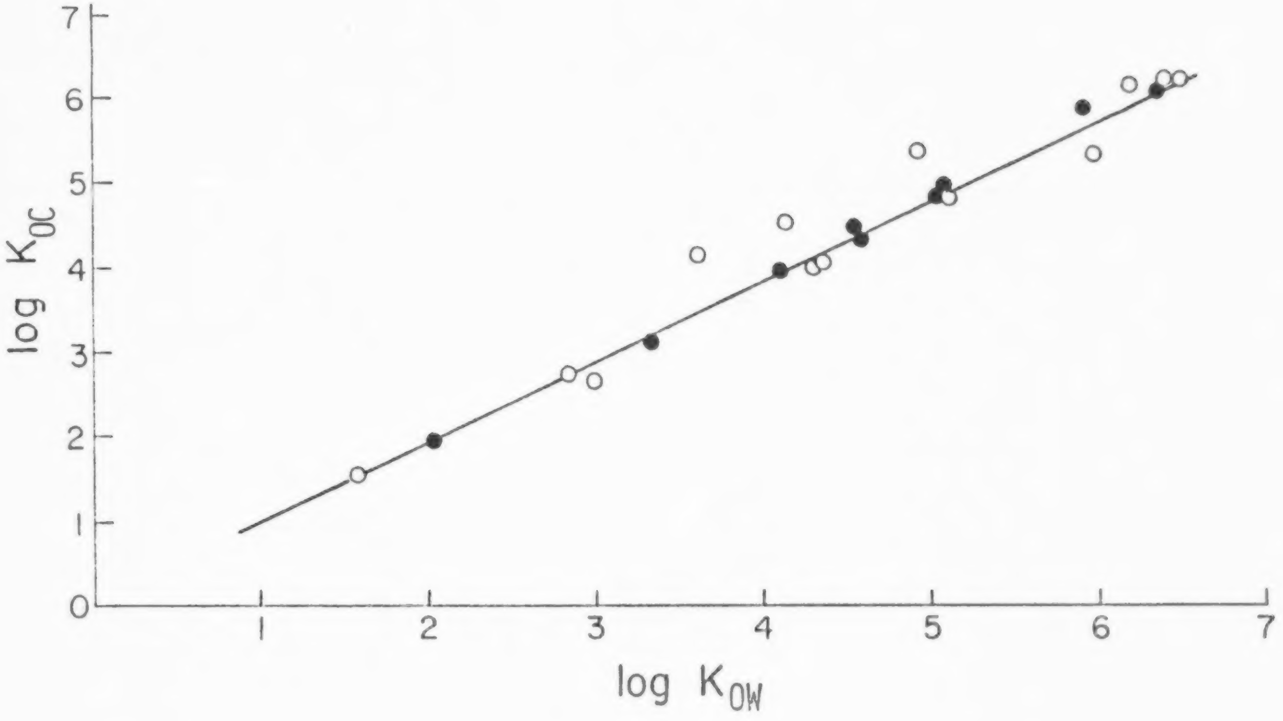


FIGURE II-5 RELATIONSHIP BETWEEN K_{OC} AND OCTANOL-WATER PARTITION COEFFICIENT (K_{OW}) OF ENERGY-RELATED ORGANIC POLLUTANTS

REFERENCE: HASSETT ET AL. (1980)

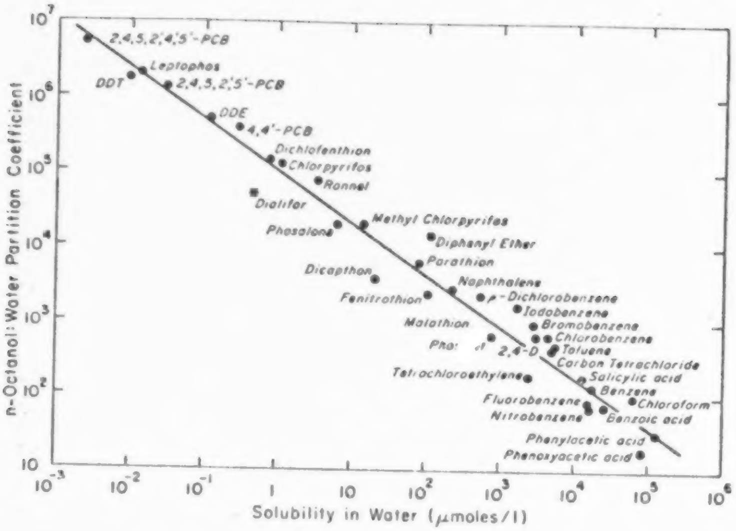
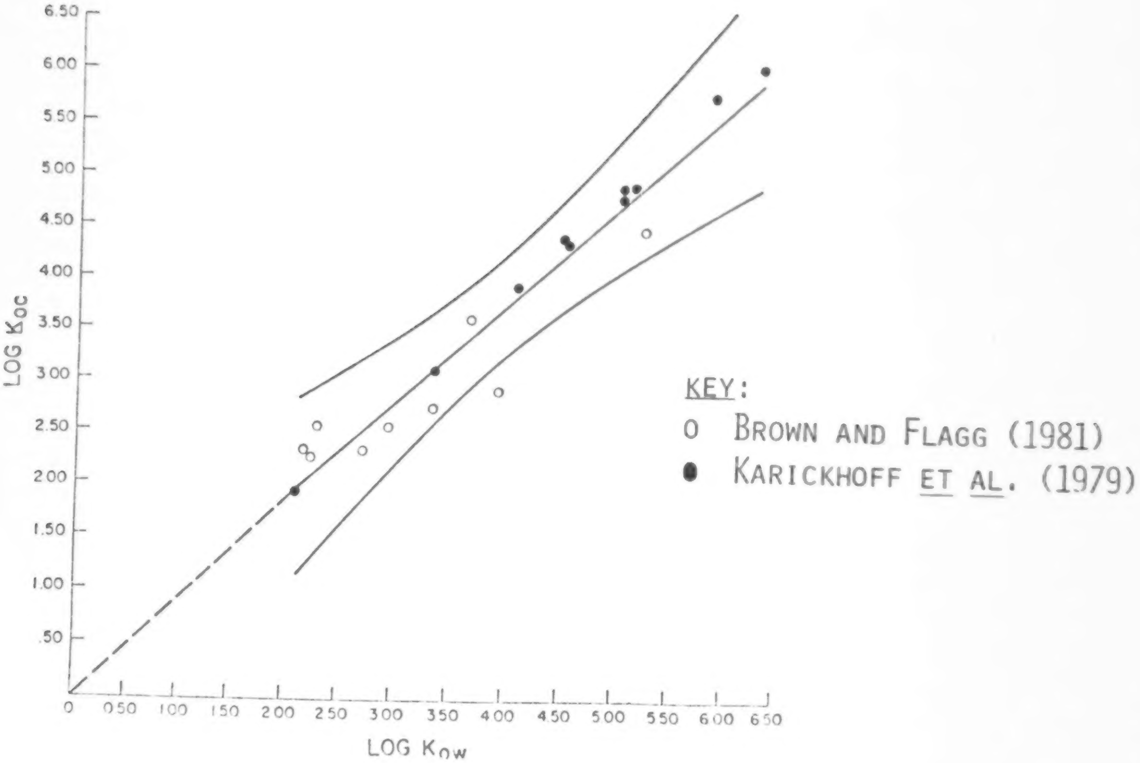


FIGURE II-6 CORRELATION OF AQUEOUS SOLUBILITY WITH OCTANOL-WATER PARTITION COEFFICIENT

REFERENCE: CHIOU _ET AL_. (1977)



Note: The actual error bands for this figure are probably greater than indicated here due to error in the measurement of K_{ow}.

FIGURE II-7 RELATIONSHIP BETWEEN K_{OC} AND K_{OW} FOR COARSE SILT

the octanol-water partition coefficient. Tables II-5 through II-9 shown earlier contain K_{ow} values for a number of compounds. Then based on an estimate of organic carbon fraction in the fine and coarse sediments, K_p can be estimated from Equation II-17.

2.3.2.5 Solute and Sorbate Fractions

The relative amount of pollutant sorbed and dissolved depends on both the suspended sediment concentration and the partition coefficient, and at equilibrium is given by:

$$\alpha_w \equiv \frac{C_w}{C_T} = \frac{1}{1+K_p S} \tag{II-22}$$

where

C_w = total dissolved phase concentration

$C_T = C_w + C_S$

$C_S = XS$

K_p = partition coefficient

S = suspended sediment concentration, on a part per part basis

X = mass of sorbed pollutant per mass of suspended sediment.

Equation II-22 can be illustrated more vividly by tabulating ranges of K_p and S values. Table II-14 shows this information. Partition coefficients and suspended sediment concentrations range from 10^0 to 10^4. For the lowest value of the partition coefficient nearly all of the pollutant is present in the dissolved form, regardless of the suspended sediment concentration. Also, for low suspended sediment concentrations, nearly all of the pollutant is dissolved, unless the partition coefficient is extremely large. When relatively high partition coefficients and sediment concentrations occur simultaneously, then most of the pollutant present exists as sorbate. For

TABLE II-14

RELATIONSHIP OF DISSOLVED AND SORBED PHASE POLLUTANT CONCENTRATIONS TO PARTITION COEFFICIENT AND SEDIMENT CONCENTRATION

			If C_T = 100 ppb		
K_p	S (ppm)	C_w/C_T	C_w=	X =	C_S =
10^0	1	1.0	100.	100.	0.0
	10	1.0	100.	100.	0.0
	100	1.0	100.	100.	0.0
	1000	1.0	100.	100.	0.0
	10000	1.0	99.	99.	1.0
10^1	1	1.0	100.	$1x10^3$	0.0
	10	1.0	100.	$1x10^3$	0.0
	100	1.0	99.9	999.	0.1
	1000	1.0	99.0	990.	1.0
	10000	0.9	90.9	909.	9.1
10^2	1	1.0	100.	$1x10^4$	0.0
	10	1.0	99.9	$1x10^4$	0.1
	100	1.0	99.0	$9.9x10^3$	1.0
	1000	0.9	90.9	$9.1x10^3$	9.1
	10000	0.5	50.	$5x10^3$	50.
10^3	1	1.0	99.9	$1x10^5$	0.1
	10	1.0	99.0	$9.9x10^4$	1.0
	100	0.9	90.9	$9.1x10^4$	9.1
	1000	0.5	50.	$5x10^4$	50.
	10000	0.1	9.1	$9x10^3$	90.9
10^4	1	1.0	99.0	$9.9x10^5$	1.0
	10	0.9	90.9	$9.1x10^5$	9.1
	100	0.5	50.	$5x10^5$	50.
	1000	0.1	9.1	$9.1x10^4$	90.9
	10000	0.0	1.0	$9.9x10^3$	99.0

all the cases shown, X is high which indicates that the mass sorbed per unit mass of sediment present can be high while C_s is simultaneously low.

EXAMPLE II-3

Determine the fraction of benzo(a)pyrene that is dissolved in a system containing 300 ppm suspended solids. The suspended sediments are 70 percent fines (d <50 μm) and the weight fraction of organic carbon is 10 percent of the fines and 5 percent of the sand fraction.

From Table II-9, the solubility of benzo(a)pyrene is 0.0038 mg/l, and the octanol-water partition coefficient is 10^6. If, for the moment, the octanol-water partition coefficient is ignored, Equation II-20 can be used to predict K_{ow} based on solubility. The solubility of 0.0038 mg/l must be converted to μmole/l:

$$S_w = (0.0038 \text{ mg/l})\ (10^{-3} \text{ g/mg})\ \left(\frac{1 \text{ mole}}{252 \text{ gm}}\right)\ \left(10^6 \frac{\mu\text{mole}}{\text{mole}}\right)$$
$$= 0.015\ \mu\text{mole/l}$$

From Equation II-20, the predicted octanol-water partition coefficient is:

$$\log K_{ow} = 5.00 - 0.670 \log (.015) = 6.22$$

so $K_{ow} = 10^{6.22}$, which is acceptably close to the tabulated value of 10^6.

Using the tabulated K_{ow}, K_{oc} is computed from Equation II-18:

$$K_{oc} = 0.63\ 10^6 = 630{,}000$$

From Equation II-17, the partition coefficient becomes:

$$K_p = 630{,}000\ [0.2\ (1-.7)\ (.05) + 0.7\ (.10)]$$
$$= 46{,}000$$

The suspended sediment concentration for the system is 300 ppm, or $300 \cdot 10^{-6}$ parts per part. Using Equation II-22, the fraction of benzo(a)pyrene which is dissolved is:

$$\frac{C_w}{C_T} = \frac{1}{1 + 300 \cdot 10^{-6} \cdot 46{,}000} = 0.067 \text{ or about 7 percent}$$

Consequently, most of the benzo(a)pyrene is present as sorbate.

END OF EXAMPLE II-3

2.4 TRANSPORT PROCESSES

2.4.1 Solubility Limits

The concentration of a compound in a natural water, and therefore the rate of transport by that water, can be limited by its equilibrium solubility. The aqueous solubility of organic compounds ranges widely:

Compound	Aqueous Solubility at 25°C (mass which will dissolve in 1 liter of water)
Sucrose	2,000,000 milligrams
Benzene	2,000 milligrams
Toxaphene	2 milligrams
Chrysene	0.002 milligrams

Non-polar compounds have limited solubilities in polar solvents such as water. The solubility of toxic organic compounds is generally much lower than for inorganic salts. Equilibrium solubilities for toxic organic compounds are given in Tables II-5 through II-9. Solubility increases with temperature for most organic compounds, typically by a factor of about 3 from 0°C to 30°C.

Organics are generally less soluble in sea water than in fresh water as can be seen in the tabulations below (Rossi and Thomas, 1981):

Compound	Solubility at 25°C Distilled Water	Sea Water
Toluene	507 μg/l	419 μg/l
Acenapthene	2.41 μg/l	1.84 μg/l
Pyrene	0.13 μg/l	0.09 μg/l

In the absence of colloids or micelles, the maximum amount of a toxic organic substance which can be held in the water column under equilibrium conditions is just the aqueous equilibrium solubility S_w, plus the equilibrium amount of solute sorbed on suspended matter:

$$C_T = S_w + f_s(S_w) \qquad \text{(II-23)}$$

where C_T = total amount of compound which can be held in a natural water at equilibrium conditions, μg liter^{-1}

S_w = equilibrium aqueous solubility, μg liter^{-1}

$f_s(S_w)$ = equilibrium amount of sorbate on suspended matter; a function of S_w. f_s is the sorption isotherm function.

If a linear sorption isotherm is used, as is commonly the case for trace constituents (see Section 2.3.2), the above expression becomes:

$$C_T \leq S_w (1 + K_p S) \qquad \text{(II-24)}$$

where K_p = linear partition coefficient (see Section 2.3.2.4), liter Kg^{-1}

S = the "concentration" of suspended matter (sorbent), Kg liter^{-1}

The inequality results in the above equation because at high solute concentrations linear isotherms overpredict the amount of solute sorbed. The use of linear sorption isotherms (a common practice for trace constituents) is adequate at pollutant concentrations which are equal to, or less than, one half of the equilibrium solubility. When linear sorption isotherms are used, e.g. those with the simple partition coefficient approach (K_p) presented in Section 2.3.2, one must then check to insure that the aqueous pollutant concentration is less than or equal to one-half of its equilibrium solubility.

2.4.2 Volatilization

2.4.2.1 Introduction

Volatilization is defined as the transfer of matter from the dissolved to the gaseous phase. A considerable number of toxic substances volatilize in the natural environment. Volatilization rates depend on the properties of the toxicant and on the characteristics of the water body. If a toxicant is "highly volatile", then obviously volatilization is an important process affecting the fate of the toxicant. However, even for toxicants which are considerably less volatile, volatilization cannot always be ignored. This is because the fate of a toxicant is governed by a variety of processes. If volatilization proceeds as fast as other competing mechanisims, even though all the rates might be slow, then volatilization will influence the fate of the toxicant.

Methods will be provided in this section to predict the volatilization rate for toxic organic substances, which volatilize according to the following relationship:

$$\frac{\partial C}{\partial t} = \frac{-k_v}{Z}\left(C - \frac{P}{K_H}\right) = -k_v'\left(C - \frac{P}{K_H}\right) \qquad \text{(II-25)}$$

where

C = concentration of toxicant in dissolved phase (concentration of solute)

k_v = volatilization rate constant in units of length/time

k_v' = volatilization rate constant in mixed water body in units of time^{-1}

Z = mixed depth of water body

P = partial pressure of toxicant in atmosphere above the waterbody being investigated.

K_H = Henry's Law constant

For many applications the partial pressure of the compound in the atmosphere is zero, so that Equation II-25 simplifies to:

$$\frac{\partial C}{\partial t} = -k_v' C \qquad \text{(II-26)}$$

An alternate form of Equation II-26 is in terms of the total pollutant concentration, C_T, and the site specific volatilization rate constant, k_{vm}:

$$\frac{\partial C_T}{\partial t} = -k_{vm} C_T \qquad \text{(II-27)}$$

where

$$k_{vm} = \frac{k_v \alpha_w}{Z} \qquad \text{(II-28)}$$

α_w = fraction of toxicant present in dissolved phase

The following sections will illustrate how to predict the volatilization rate for toxicants of either low or high volatility. But first, a brief discussion of Henry's Law is required.

2.4.2.2 Henry's Law

Henry's Law is an expression which relates the concentration of a chemical dissolved in the aqueous phase to the concentration (or pressure) of the chemical in the gaseous phase when the two phases are at equilibrium with each other. One method of commonly expressing Henry's Law is:

$$P = K_H C_w \qquad \text{(II-29)}$$

where

P = equilibrium partial pressure of pollutant in atmosphere above the water, atm

C_w = equilibrium concentration of pollutant in the water, mole/m^3

K_H = Henry's Law constant, atm m^3/mole

Henry's Law in this form is valid for pollutants present in concentrations up to 0.02 expressed as a mole fraction. For compounds with molecular weights greater than 50 g/mole, a mole fraction of 0.02 represents a concentration of at least 55,000 mg/l. Typically toxic pollutant levels in the environment are present at levels far below this concentration.

Table II-15 contains values of Henry's Law constants for a number of selected hydrocarbons. In the table, Henry's Law constant is expressed in units of atm m^3/mole. However, in the literature Henry's Law constant can be defined in numerous ways. A second, widely used method of defining Henry's Law constant is:

$$K_H' = \frac{C_a}{C_w} \qquad \text{(II-30)}$$

where

C_a = molar concentration in air, mole/m^3

K_H' = alternate form of Henry's Law constant, dimensionless.

Equations II-29 and II-30 are related as follows:

$$K_H' = \frac{K_H}{R_u T} = \frac{K_H}{8.2 \times 10^{-5}\ T} = 41.6\, K_H \text{ at } 20^\circ\mathrm{C} \qquad \text{(II-31)}$$

where

T = temperature of water, $^\circ$K.

This relationship is based on the ideal gas law. Equation II-31 is useful because of the frequent necessity to convert literature data from one set of units to another.

TABLE II-15

HENRY'S LAW CONSTANT FOR SELECTED HYDROCARBONS

Olefins and Acetylenes	K_H Henry's Law Constant (atm-m^3/mole	k_v (cm/hr)[a]	Aromatics	K_H Henry's Law Constant (atm-m^3/mole	k_v (cm/hr)[a]
Ethene (*g*)	0.214	20.	Benzene (ℓ)	5.49×10^{-3}	19.4
Propene (*g*)	0.232	20.	Toluene (ℓ)	6.66×10^{-3}	19.5
1-Butene (*g*)	0.268	20.	Ethyl benzene (ℓ)	8.73×10^{-3}	19.6
1-Pentene (ℓ)	0.398	20.	*o*-Xylene (ℓ)	5.27×10^{-3}	19.4
1-Hexene (ℓ)	0.412	20.	Isopropylbenzene (ℓ)	1.45×10^{-2}	19.8
2-Heptene (ℓ)	0.418	20.	Naphthalene (*s*)	4.25×10^{-4}	14.5
1-Octene (ℓ)	0.905	20.	Biphenyl (*s*)	6.36×10^{-4}	16.0
Propyne (*g*)	0.0110	19.8	Acenaphthene (*s*)	2.28×10^{-4}	11.7
1-Butyne (*g*)	0.0194	20.	Fluorene (*s*)	2.35×10^{-4}	11.9
			Anthracene (*s*)	1.65×10^{-3}	18.2
			Phenanthrene (*s*)	1.48×10^{-4}	9.6
Cycloalkanes Branched-Chain Alkanes			*n*-Alkane		
Cyclopentane (ℓ)	0.187	20.	Methane (*g*)[a]	0.665	20.
Cyclohexane (ℓ)	0.196	20.	Ethane (*g*)	0.499	20.
Methylcyclopentane (ℓ)	0.362	20.	Propane (*g*)	0.707	20.
Methylcyclohexane (ℓ)	0.428	20.	*n*-Butane (*g*)	0.947	20.
Propylcyclopentane (ℓ)	0.893	20.	*n*-Pentane (ℓ)	1.26	20.
Isobutane (*g*)	1.24	20.	*n*-Hexane (ℓ)	1.85	20.
Isopentane (ℓ)	1.364	20.	*n*-Heptane (ℓ)	2.07	20.
2-Methylpentane (ℓ)	1.73	20.	*n*-Octane (ℓ)	3.22	20.
2-Methylhexane (ℓ)	3.42	20.	*n*-Nonane (ℓ)	3.29	20.
2,2-Dimethylpentane (ℓ)	3.15	20.	Decane (ℓ)	4.93	20.
3-Methylheptane (ℓ)	3.71	20.	Dodecane (ℓ)	7.12	20.
2,2,4-Trimethylpentane (ℓ)	3.04	20.	Tetradecane (ℓ)	1.14	20.
4-Methyloctane (ℓ)	9.936	20.			20.
Polychlorinated Biphenyls			Pesticides		
Aroclor 1242	5.7×10^{-4}	15.6	DDT	3.9×10^{-5}	3.9
Aroclor 1248	3.5×10^{-3}	18.9	Lindane	4.9×10^{-7}	0.06
Aroclor 1254	2.8×10^{-3}	18.9	Dieldrin	2.0×10^{-7}	0.02
Aroclor 1260	7.1×10^{-3}	19.6	Aldrin	1.4×10^{-5}	0.60
			Endrin	4.6×10^{-7}	0.06
			Heptachlor	1.5×10^{-3}	18.
			Chlordane	5×10^{-5}	4.8
			Toxaphene	0.1	19.8

---

[a] These are estimated values based on k_l = 20 cm/hr and k_g = 3000 cm/hr.

Henry's Law constant can be estimated for slightly soluble compounds (mole fraction ≤ 0.02) by the following expression:

$$K_H \text{ (atm·m}^3\text{/mole)} = \frac{P_s \times MW}{760 \times S_w} \qquad \text{(II-32)}$$

where

P_s = saturation vapor pressure of pure compound in Torr

MW = molecular weight

S_w = solubility in water in ppm

Tables II-5 through II-9 presented vapor pressure and solubility data for the organic priority pollutants, which can be used to predict Henry's Law constant. Although Equation II-32 is not valid for highly soluble chemicals, generally the toxicants of interest here are only slightly soluble, so that the expression is adequate. The dimensionless form of Henry's Law constant is expressable as:

$$K_H' = \frac{16.04\ P_s \times MW}{S_w \times T} \qquad \text{(II-33)}$$

where all variables have been previously defined.

EXAMPLE II-4

Henry's Law Constant for Chloroform

Calculate Henry's Law constant in the two forms expressed by Equations II-32 and II-33. Chloroform (also called trichloromethane or $CHCl_3$) has the following properties:

- vapor pressure = 150 Torr (from Table II-5)
- solubility = 8200 ppm at 20°C (from Table II-5)

- Molecular weight = 12 (carbon)
  1 (hydrogen)
  3 x 35.5 (chlorine)
  Sum = 119

From Equation II-32,

$$K_H = \frac{150\times119}{760\times8200} = 2.86 \times 10^{-3}\ \text{atm}\cdot\text{m}^3/\text{mole}$$

From Equation II-33, at 20^{o}C (293^{o}K):

$$K'_H = \frac{16.04\times150\times119}{8200\times293} = 0.12$$

Henry's constant, expressed as K'_H, had been found experimentally to be 0.12, the same as predicted here.

END OF EXAMPLE II-4

2.4.2.3 Two Film Theory of Volatilization

When a chemical volatilizes from water, the process can be visualized as a mass transfer occurring over several distinct steps. Figure II-8 presents a schematic representation of the process. The concentration of the chemical is C in the bulk liquid solution. As the chemical moves upward in the bulk solution it moves through a thin "liquid film" where a concentration gradient develops because the transfer rate is limited by diffusion. The dissolved chemical then volatilizes and passes through a thin "gas film", where again transfer may be limited, before reaching the bulk vapor phase.

At the interface between the gas and liquid films the concentration in the liquid (C_i) and in the gas (P_{ci}, expressed as partial pressure) are assumed to be in equilibrium and to obey Henry's Law:

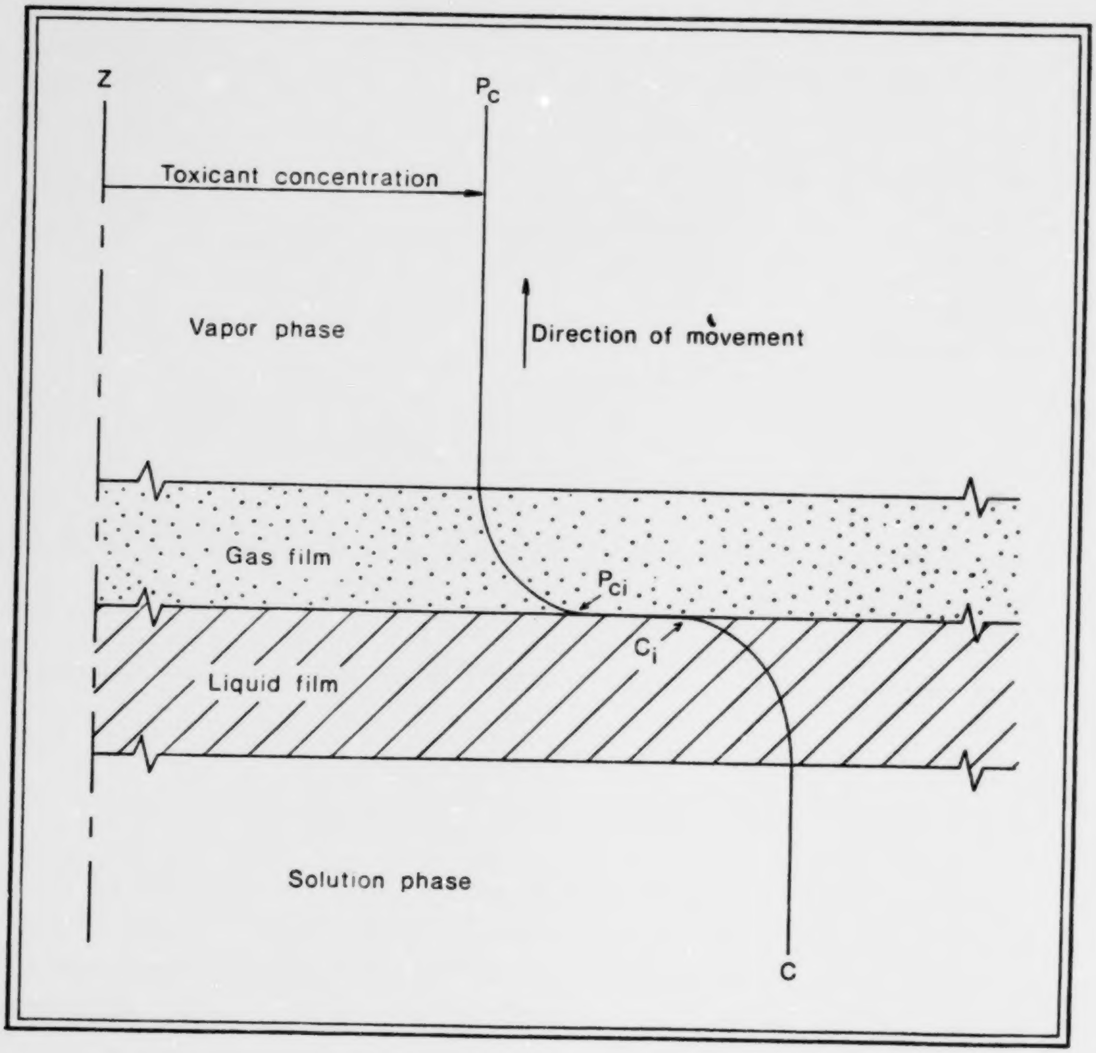

Z
P_c
Toxicant concentration
Vapor phase
Direction of movement
Gas film
P_{ci}
C_i
Liquid film
Solution phase
C

FIGURE II-8 SCHEMATIC REPRESENTATION OF VOLATILIZATION FROM SOLUTION PHASE TO LIQUID PHASE

$$P_{ci} = K_H C_i \tag{II-34}$$

In the absence of net accumulation at the interface the mass flux from one phase must equal the mass flux from the other, or

$$F_z = \frac{-k_{gi}}{R_u T} (P_c - P_{ci}) = k_{li} (C - C_i) \tag{II-35}$$

where

F_z = flux of chemical in z direction

k_{gi} = mass transfer coefficient in the gas phase across "gas film"

k_{li} = mass transfer coefficient in the liquid phase across "liquid film"

and P_c, P_{ci}, C, C_i are defined in Figure II-8. Since it is not convenient to measure the partial pressure and concentration at the interface, it is worthwhile to develop expressions for bulk transfer coefficients, given by:

$$F_z = \frac{-k_{vg}}{R_u T} (P_c - P_c') = k_{vl} (C - S_p) \tag{II-36}$$

where

k_{vg} = overall volatilization rate defined for the gaseous phase

k_{vl} = overall volatilization rate defined for the liquid phase

S_p = saturation concentration of chemical in equilibrium with P_c

P_c' = partial pressure in equilibrium with C

Combining Henry's Law equilibrium expressions with Equations II-35 and II-36 the overall volatilization rates become:

$$\frac{1}{k_{vg}} = \frac{1}{R_u T} \cdot \frac{K_H}{k_{li}} + \frac{1}{k_{gi}} \qquad \text{(II-37)}$$

and

$$\frac{1}{k_{vl}} = \frac{1}{k_{li}} + \frac{R_u T}{K_H k_{gi}} \qquad \text{(II-38)}$$

Of the two expressions, normally Equation II-38 is more useful for the purposes of this document because the pollutants being analyzed are in the aqueous phase. To simplify terminology Equation II-38 will be rewritten as:

$$\frac{1}{k_v} = \frac{1}{k_l} + \frac{R_u T}{K_H k_g} \qquad \text{(II-39a)}$$

or:

$$\frac{1}{k_v} = \frac{1}{k_l} + \frac{1}{K_H' k_g} \qquad \text{(II-39b)}$$

where the second subscripts to each variable have been dropped. The volatilization rate, k_v, is the same as shown earlier in Equation II-25 and depends on k_g, K_H', and k_l.

There are two special cases of Equation II-39, depending on the value of Henry's Law constant. They are:

$$k_v = \begin{cases} k_l, \text{ for large } K_H' \text{ (liquid-phase limited)} & \text{(II-40a)} \\ K_H' k_g, \text{ for small } K_H' \text{ (gas-phase limited)} & \text{(II-40b)} \end{cases}$$

To make Equation II-40 usable, "large" and "small" values of K_H' have to be defined. For cases when the liquid phase is limiting the transfer rate, a large fraction, R, of the total resistance exists in the liquid phase, or:

$$\frac{1}{k_l} = R\left(\frac{1}{k_v}\right) = R\left(\frac{1}{k_l} + \frac{1}{K_H' k_g}\right) \qquad \text{(II-41)}$$

Similarly when the gas phase is limiting:

$$\frac{1}{K_H' k_g} = R\left(\frac{1}{k_v}\right) = R\left(\frac{1}{k_l} + \frac{1}{K_H' k_g}\right) \qquad \text{(II-42)}$$

Equations II-41 and II-42 can be rearranged to express Henry's Law constant explicity:

$$K_H' = \begin{cases} \dfrac{k_l}{k_g}\,\dfrac{R}{1-R}\text{, for liquid-phase limited} & \text{(II-43a)} \\[2ex] \dfrac{k_l}{k_g}\,\dfrac{1-R}{R}\text{, for gas-phase limited} & \text{(II-43b)} \end{cases}$$

At this point values for R, k_l, and k_g must be specified. "Typical" values of k_g and k_l for surface waters are in the range of 20 cm/hr and 3,000 cm/hr, respectively. For R values of 0.83, 0.90, and 0.95, the phase limiting values of Henry's Law constants, converted to units of atm·m^3/mole using Equation II-31, are as follows:

	Henry's Constant (atm·m^3/mole)	
R	Liquid-phase Limited	Gas-phase Limited
0.83	7.8×10^{-4}	3.3×10^{-5}
0.90	1.4×10^{-3}	1.8×10^{-5}
0.95	3×10^{-3}	8.4×10^{-6}

Hence, for Henry's Law constants larger than about 1.0×10^{-3} atm m^3/mole most of the resistance to volatilization lies in the liquid phase, and for Henry's Law constants less than about 1.0×10^{-5} atm m^3/mole, most of the resistance lies in the gas phase. When either of the two phases controls the volatilization rate, then the simplified Equation II-40 can be used in lieu of Equation II-39. The data in the tables presented earlier can be used to predict Henry's Law constant and then to decide whether the gas or liquid phase limits volatilization.

Based on the two-film model there are two methods which can be used to estimate volatilization rates. One approach is considerably more simple than the other. The simpler approach is based on the following reasoning. Using "typical" values of k_l and k_g, k_v can be estimated based solely on K_H

as the independent variable, where K_H is allowed to vary over its potential range of values. As Table II-16 shows, K_H can vary by at least seven orders of magnitude. Based on this variability of Henry's Law constant, Table II-17 presents the associated volatilization rates. As Henry's Law constant increases, the volatilization rate approaches 20 cm/hr, the liquid phase limiting rate. As Henry's Law constant decreases, so does the volatilization rate, with the lower limit being zero.

The second method of predicting k_v is based on finding k_g and k_l individually, rather than assuming typical values. The gas-phase transfer rate can be found based on the evaporation rate of water as outlined in Mills (1981). Mills showed that:

$$k_g' = 700\ V \tag{II-44}$$

where

k_g' = gas transfer rate for water vapor, cm/hr

V = wind speed, m/sec

This expression was derived from an empirical relationship shown in Linsley *et al.*, (1979) for the evaporation of water. Liss (1973) conducted measurements in an experimental basin and found that:

$$k_g' = 1000\ V \tag{II-45}$$

where the units are the same in Equation II-44. Considering that the approaches used to develop Equations II-44 and II-45 are different, their agreement is good.

The values of k_g and k_g' are related by penetration theory (Bird *et al.*, 1960) as follows:

$$k_g = \left(\frac{D_a}{D_{wv}}\right)^{\frac{1}{2}} k_g' \tag{II-46}$$

TABLE II-16

HENRY'S LAW CONSTANTS FOR SELECTED COMPOUNDS

Compound	Henry's Law Constant (atm·m^3/mole)
Vinyl Chloride	3.7
Carbon Tetrachloride	2×10^{-2}
Toluene	6.7×10^{-3}
Aroclor 1254	2.8×10^{-3}
Flourene	2.4×10^{-4}
DDT	3.9×10^{-5}
Dieldrin	2.0×10^{-7}

TABLE II-17

TYPICAL VALUES OF POLLUTANT VOLATILIZATION RATES IN SURFACE WATERS

K_H(atm·m^3/mole)	K_H' (dimensionless)	k_v (cm/hr)*
10^0	41.6	20.
10^{-1}	4.2	20.
10^{-2}	4.2×10^{-1}	19.7
10^{-3}	4.2×10^{-2}	17.3
10^{-4}	4.2×10^{-3}	7.7
10^{-5}	4.2×10^{-4}	1.2
10^{-6}	4.2×10^{-5}	0.1
10^{-7}	4.2×10^{-6}	0.01

*using k_g = 3000 cm/hr
k_l = 20 cm/hr

where

D_a = diffusion coefficient of pollutant in air

D_{wv} = diffusion coefficient of water vapor in air

Diffusion coefficient data can be found in such references as Perry and Chilton (1973), or estimated using the Wilke-Chang method, also in Perry and Chilton. If an analytical method is used to estimate diffusion coefficients, note that it is easier to predict the ratio of two diffusion coefficients than to predict each coefficient individually because some of the required information cancels out of the ratio, and consequently is not needed at all.

In many cases it is acceptable to approximate the ratio of diffusion coefficients as follows:

$$\frac{D_a}{D_{wv}} = \left(\frac{18}{MW}\right)^{\frac{1}{2}} \qquad \text{(II-47)}$$

where

MW = molecular weight of pollutant

Table II-18 illustrates the difference between calculating the diffusion coefficient ratio by using tabulated data from Perry and Chilton and by using Equation II-47. The percent differences between the ratios range from 1 to 27 percent and average 15 percent. This agreement is acceptable for screening purposes. Combining Equations II-46, II-44, and II-47, the final expression for k_g (in units of cm/hr) is:

$$k_g = 700 \left(\frac{18}{MW}\right)^{\frac{1}{4}} V \qquad \text{(II-48)}$$

This expression is valid for rivers, lakes, and estuaries.

The liquid phase transfer coefficient k_l can be predicted based on the reaeration rate, k_a, for the system. The relationship proposed by Smith et al. (1981) is:

TABLE II-18

COMPARISON OF TABULATED AND PREDICTED VALUES OF DIFFUSION COEFFICIENTS FOR SELECTED POLLUTANTS

		Diffusion Coefficient		Perry & Chilton	Predicted:	
Pollutant	Molecular Weight	Perry & Chilton (cm^2/sec)	Predicted (cm^2/sec)	$\left(\frac{D}{D_{wv}}\right)^{\frac{1}{2}}$	$\left(\frac{D}{D_{wv}}\right)^{\frac{1}{2}}$	Percent Difference
Chlorobenzene	113	0.075	0.088	.58	.63	9
Toluene	92	0.076	0.097	.59	.66	12
Chloroform	119	0.091	0.086	.64	.63	1
Naphthalene	128	0.051	0.083	.48	.61	27
Anthracene	178	0.042	0.070	.44	.56	27
Benzene	78	0.077	0.106	.59	.69	17

$$k_1 = \left(\frac{D_w}{D_{O_2}}\right)^n k_a' \quad , \quad 0.5 \leq n \leq 1 \qquad \text{(II-49)}$$

where

D_w = diffusion coefficient of pollutant in water

D_{O_2} = diffusion coefficient of dissolved oxygen in water

k_a' = surface transfer rate of dissolved oxygen, expressed in the same units as k_1.

In other chapters of this report, the reaeration rate is presented as k_a, defined as:

$$k_a = k_a'/Z \qquad \text{(II-50)}$$

where

Z = mixed depth of water body

For rivers the mixed depth is the total depth, while for estuaries the mixed depth is the total depth only if the estuary is well mixed. Otherwise, it is the depth to the pycnocline. Similarly for lakes, the mixed depth can be less than the total depth, and can be chosen to be the depth of the epilimnion.

The exponent n varies as a function of the theorical approach used to develop Equation II-49. If film theory is used, i.e. the film is considered to be a laminar sublayer, then n = 1. If penetration or surface renewal theory is used, n = 0.5. Using experimental approaches, researchers have found n to vary from 0.5 to 1.0. Since the movement of water in natural water bodies is generally turbulent, the parameter n can be chosen to be 0.5.

Perry and Chilton (1973) provide data and methods to predict the diffusion coefficient of a pollutant in water. The Othner-Thakor relationship, described in Smith et al. (1981) can also be used. As an approximate approach, by using the square root of the molecular weights the following expression results:

$$k_l = \left(\frac{32}{MW}\right)^{1/4} k_a' \qquad \text{(II-51)}$$

A recent study (Rathbun and Tai, 1981) used a tracer technique to predict the volatilization rates of four priority pollutants from 12 different rivers. That study provides an opportunity to compare, even if only to a limited degree, some of the methods presented here against field results. Table II-19 briefly summarizes the results of Rathbun and Tai (1981). As shown by the values of Henry's Law constant for the four pollutants, each pollutant is liquid phase limited, since all Henry's Law constants exceed 1.0×10^{-3} atm m^3/mole. The study results were unable to predict differences in volatilization rates for the four pollutants, and found that the best predictive expression was:

$$k_v = 0.655\, k_a'$$

Based on Equation II-51 the screening methods predict:

$$k_v = 0.7\, k_a' \text{ to } 0.8\, k_a'$$

where the range reflects the variability in molecular weight among the four pollutants.

If the default value of 20 cm/hr, suggested earlier in this section were used as a rough estimate of the volatilization rate for liquid phase limited pollutants, this value would fall within the observed range of 1.5 to 24 cm/hr. It appears that the screening methods presented here generate acceptable estimates of volatilization rates.

TABLE II-19

RESULTS OF A STUDY TO DIRECTLY DETERMINE VOLATILIZATION RATES OF SEVERAL PRIORITY POLLUTANTS IN RIVERS[a]

Pollutant	Henry's Constant ($atm \cdot m^3/mole$)	Molecular Weight
Benzene	5.5×10^{-3}	119
Chloroform	2.9×10^{-3}	78
Methylene Chloride	2.7×10^{-3}	85
Toluene	6.7×10^{-3}	92

Study results showed: $k_v = 0.655\ k_a'$

Range of values for 12 rivers: 1.5 to 24 cm/hr

Screening method predicts: $k_v = 0.7\ k_a'$ to $0.8\ k_a'$

---

[a] Rathbun, R.E. and D.Y. Tai. 1981. Techniques for Determining the Volatilization Coefficients of Priority Pollutants in Streams. Water Research, Volume 15, pp. 243-250.

2.4.2.4 Volatilization Half-Life

Numerous researchers have in the past calculated the volatilization half-life of toxicants under controlled laboratory conditions. The result of some of this work was shown earlier in Tables II-5 through II-9. Typically researchers have used the following expression to calculate the half-life:

$$t_{\frac{1}{2}} = \frac{0.693\,Z}{k_v} \qquad \text{(II-52)}$$

where

$t_{\frac{1}{2}}$ = half-life (time required for the concentration of the contaminant to decrease by half)

It is important to understand that the volatilization half-life of a toxicant varies according to the environmental conditions. Under controlled laboratory conditions, where the depth of water is extremely small, $t_{\frac{1}{2}}$ can be extremely small. If the water depth increases by 100 fold, for example, so does $t_{\frac{1}{2}}$.

The volatilization half-life is affected by suspended solids in the system. When suspended solids are present, Equation II-52 should be modified to:

$$t_{\frac{1}{2}} = \frac{0.693\,Z}{k_v}\,(1 + SK_p) \qquad \text{(II-53)}$$

where

S = suspended solids concentration

K_p = partition coefficient

The partition coefficient is the ratio of the sorbed pollutant concentration to the dissolved phase concentration. A method to predict K_p was discussed earlier in Section 2.3.2. Since the toxicant which sorbs to the sediments is not directly available for volatilization, the total flux of volatilizing particles decreases. The following example illustrates how sorption can influence the half-life.

EXAMPLE II-5

The following data for hexachlorobenzene were obtained from Table II-8:

- solubility = 20 μg/l
- vapor pressure = 10^{-5} Torr at $20^{o}C$
- $K_{ow} \approx 10^{6}$

Under the conditions reported in the work of Mackay and Leinonen (1975)

$L = 1$ m

$k_v = 8$ cm/hr $= 8 \times 10^{-2}$ m/hr

Hence

$$t_{1/2} = \frac{0.693 \times 1}{8 \times 10^{-2}} = 8.7 \text{ hours}$$

Note that the half-life is small even though the vapor pressure is only 10^{-5} Torr. The results indicate that the vapor pressure is, by itself, not necessarily a good indicator of the importance of volatilization.

Now, consider the following conditions which might be encountered in a river:

- k_a (reaeration rate) = 0.5/day
- suspended sediment concentration = 550 ppm

- $K_p = 5 \times 10^4$
- depth = 1 m

The expression of volatilization half-life modified to account for the presence of the suspended solids is:

$$t_{\frac{1}{2}} = \frac{0.693\ Z}{k_v} (1 + S\ K_p)$$

From Equation II-51, the liquid-phase transfer rate for hexachlorobenzene is:

$$k_1 = \left(\frac{32}{285}\right)^{\frac{1}{4}} \times 0.5 \times 1 = 0.29 \text{ m/day} = 0.01 \text{ m/hr} = 1 \text{ cm/hr}$$

Henry's Law constant can be estimated based on Equation II-32.

Using the data presented earlier

$$K_H = \frac{10^{-5} \times 285}{760 \times .02} = 1.9 \times 10^{-4} \text{ atm}\cdot\text{m}^3\text{/mole} = 7.8 \cdot 10^{-3}, \text{ dimensionless}$$

Using a default value of 3,000 cm/hr for k_g, the volatilization rate is:

$$\frac{1}{k_v} = \frac{1}{1} + \frac{1}{3000 \times 7.8 \times 10^{-3}} = 1.04 \text{ cm/hr}$$

So

$$k_v \approx 1 \text{ cm/hr}$$

The half-life becomes

$$t_{\frac{1}{2}} = \frac{0.693 \times 1}{1 \times 10^{-2}} \left(1 + \frac{550}{10^6} \times 5 \times 10^4\right) = 1800 \text{ hr} = 75 \text{ days}$$

A comparison of half-lives shows that:

- t = 8.7 hours under laboratory conditions

- t = 75 days under instream conditions

This example illustrates that half-lives are not always extrapolatable from one type of system to another due to the combined difference in sorption effects and volatilization rates.

END OF EXAMPLE II-5

2.4.2.5 Flux of Volatilizing Pollutants

The preceding sections have provided techniques for predicting volatilization rates of pollutants. Obviously, if the volatilization rate of one pollutant exceeds that of a second pollutant, then the first pollutant is more volatile than the second. However, this criterion alone does not determine whether volatilization is important in a specific situation. The volatilization flux is the rate at which mass is transferred to the gaseous phase from the liquid phase and is given by the following expression:

$$\text{Flux} = k_v \quad C - \frac{P}{K_H} \tag{II-54}$$

$$= k_v C, \text{ when } P = 0 \tag{II-55}$$

where

C = concentration of pollutant in water as solute

P = partial pressure of pollutant in atmosphere.

Hence both the volatilization rate and the dissolved phase concentration have to be considered jointly to predict the flux being volatilized. Table II-20 illustrates these principals for several chemicals. The volatilization rates for these pollutants, range from a high of 20 cm/hr for carbon tetrachloride to a low of 0.02 cm/hr for dieldrin. Anthracene has a volatilization rate constant of 18 cm/hr, 90 percent as high as the volatile carbon tetrachloride. However, the solubility of anthracene in water is much lower (0.06 ppm versus 785 ppm). Hence if each of these two chemicals

TABLE II-20

RELATIVE VOLATILIZATION MASS FLUXES OF SEVERAL CHEMICALS IN SATURATED SOLUTIONS

Chemical	Henry's Law Constant ($atm \cdot m^3/mole$)	Volatilization Rate Constant (cm/hr)	Solubility (ppm)	K_{ow}	Flux Ratio[a]
Carbon Tetrachloride	2.3×10^{-2}	20.	785	400	1
DDT	3.9×10^{-5}	3.9	.002-.085	10^4-10^6	5×10^4-2×10^6
Dieldrin	2.0×10^{-4}	0.02	0.2	-	4×10^6
Phenanthrene	1.5×10^{-3}	9.6	1.0	29,000	2×10^3

---

[a] This is the ratio of volatilization flux of a saturated solution of carbon tetrachloride to the volatilization of the specified chemical.

were to volatilize from saturated solutions, the flux of carbon tetrachloride would be 15,000 times as great. The same type of comparison can be made for DDT and carbon tetrachloride. The volatilization rate constant for DDT is relatively high (about 20 percent that of carbon tetrachloride), but the solubility is so low that the ratio of volatilization flux would be about 100,000:1.

These comparisons have not considered the relative differences in sorption characteristics of the pollutants. Since only the solute volatilizes, the volatilization flux of a pollutant which is mostly sorbed to suspended material is lower than in the absence of suspended material, all other factors remaining the same. Tables II-5 through II-9 show the octanol-water partition coefficient, which provides a measure of relative importance of sorption for the four pollutants. Because both DDT and anthracene have higher octanol-water partition coefficients than does carbon tetrachloride, the ratio of volatilization of mass fluxes is likely to be even greater than calculated above for natural systems containing suspended material.

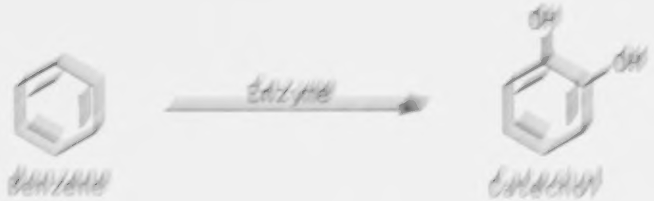
2.5 TRANSFORMATION PROCESSES

2.5.1 Biodegradation

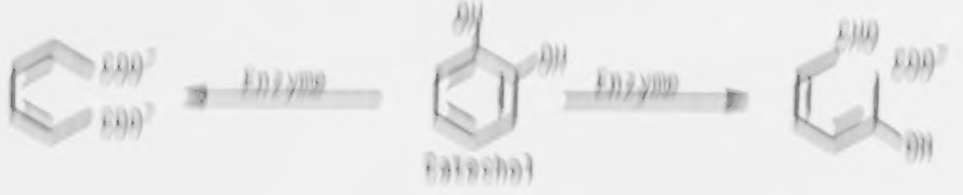
2.5.1.1 Introduction

Microorganisms are ubiquitous in the aquatic environment. Microbes are also very active chemically due to their ability to supply energy for reactions through normal metabolic processes and to catalyze reactions through enzymatic activity. Chemical reactions which proceed very slowly or not at all in the absence of biota occur at rates up to eleven orders of magnitude faster in the presence of biological enzymes. Some of the reactions catalyzed by microorganisms transform or degrade organic pollutants. Frequently, microbial degradation, or biodegradation, is the most important, if not the only process which can decompose an organic pollutant in the aquatic environment.

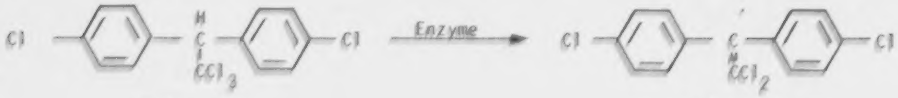
Although microbial communities catalyze countless reactions, many of them fall into a few classes of important reactions. Oxidative reactions make up one very important class of biochemical reactions. The hydroxylation of aromatic compounds, such as benzene, is an example of an oxidative reaction which generates polar compounds from non-polar ones:



An extremely important oxidative reaction unique to microbial organisms is aromatic ring fission:



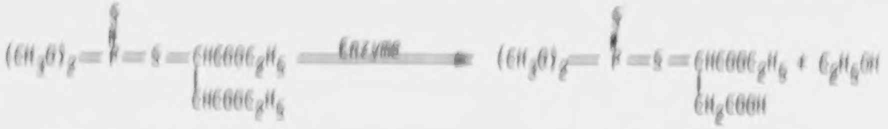
Microbes also catalyze reductive reactions. A notorious example is the dehydrochlorination of DDT to produce DDE:



DDT

DDE

Enzymes can catalyze otherwise slow hydrolytic reactions as well:



$$(CH_3O)_2-\overset{\overset{S}{\|}}{P}-S-\underset{\underset{CH_2COOC_2H_5}{|}}{CHCOOC_2H_5} \xrightarrow{\text{Enzyme}} (CH_3O)_2-\overset{\overset{S}{\|}}{P}-S-\underset{\underset{CH_2COOH}{|}}{CHCOOC_2H_5} + C_2H_5OH$$

Malathion

Malathion β-monoacid

The term "biodegradation" encompasses these and other biologically mediated processes which chemically alter a pollutant. Although each reaction causes the disappearance or primary degradation of a compound, different reactions affect the toxicity of a compound in markedly different ways (Alexander, 1980).

"Mineralization" refers to the complete degradation of an organic compound to inorganic products:

Toxic Organic Compound → CO_2 + Inorganic Products (e.g. NO_3^-, PO_4^{3-}, SO_4^{2-})

In many reactions, however, organic products remain:

"Detoxication" reactions produce innocuous metabolites from a toxic substance:

Toxic Organic Compound → Innocuous Compounds

In "activation" reactions microbes convert an innocuous compound into a toxic compound:

Innocuous Compound ➞ Toxic Compound

The "defusing" of potentially hazardous compounds occurs when biota produce an innocuous compound before the parent compound's harmful form is generated.

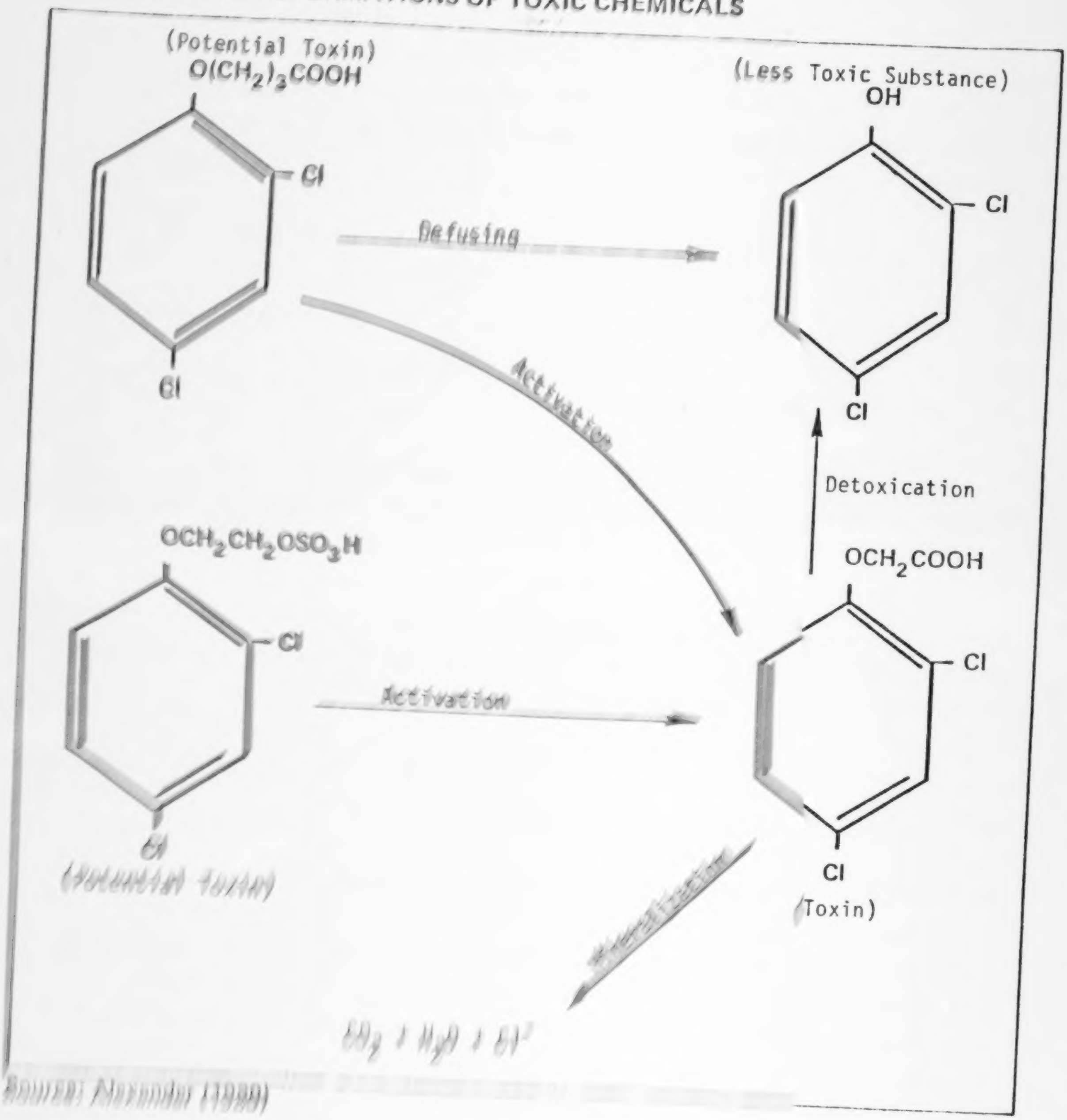
Potentially Toxic Compound ➞ Innocuous Compound

Finally, a toxic compound may be transformed chemically but still retain its toxicity. Figure II-9 illustrates some of the above types of reactions as they occur among the phenoxy herbicides.

Because of the wide variety of toxicological effects metabolic transformations may have, evaluating the impact of a compound on the environment requires a knowledge of the potential products which form. However, for the purposes of estimating the concentration of a pollutant in a natural water body, the user may simply consider biodegradation to be a decay process. Methods of estimating the rates of biodegradation constitute the subject matter of the remainder of this section.

2.5.1.2 Rates of Biodegradation in the Environment

The rate at which a compound biodegrades in the aquatic environment depends on its role in microbial metabolism. Some organic pollutants serve as food sources which provide energy and carbon for growth and cell maintenance when metabolized by a microorganism. In other cases, microorganisms transform the pollutant, but are unable to derive energy for growth from the reaction. These two metabolic patterns, growth metabolism and cometabolism, exhibit distinct characteristics and rates of degradation. Because of the important differences between these two types of biodegradation, they are treated separately in the following discussion.


MICROBIAL TRANSFORMATIONS OF TOXIC CHEMICALS

(Potential Toxin)
O(CH2)3COOH
Cl
Cl
Defusing
(Less Toxic Substance)
OH
Cl
Cl
Activation
Detoxication
OCH2CH2OSO3H
Cl
Activation
OCH2COOH
Cl
Cl
(Potential Toxin)
Mineralization
Cl
(Toxin)
CO2 + H2O + Cl-

Source: Alexander (1980)

FIGURE II-9 MICROBIAL TRANSFORMATIONS OF PHENOXY HERBICIDES

2.5.1.2.1 Metabolism of Growth Substances.

Heterotrophic bacteria degrade certain organic compounds to provide the energy and carbon required for their growth. Many toxic substances function as growth substrates for bacteria in a manner similar to naturally occurring organic compounds. These growth substrates are identifiable by their ability to serve as the sole carbon source for a bacterial culture. The metabolic transformation of these growth substrates generally results in relatively complete degradation or mineralization, thus detoxifying toxic growth substrates. The detoxifying effect and relatively rapid rates of growth metabolism imply that potential growth substrates pose a lesser threat to the environment than compounds which cannot be used in this way (Tiedje, 1980).

Before the utilization of a compound can begin, the microbial community must adapt itself to the chemical. Investigations of biodegradation of a compound to which the biota have not been recently exposed, both in the field (Spain _et al_. 1980), and in the laboratory (Shamat and Maier, 1980), have shown the existence of a lag time (lag phase) of 2 to 50 days before the microbial community acclimates. Since the degradation of a growth substrate is relatively rapid once a microbial population has adapted to it, Tiedje (1980) has suggested that the primary concern in assessing biodegradation of such substances should be the conditions and time period required for adaptation or acclimation.

The lag time depends on several biological and environmental constraints. The primary contraint is the development of a sufficiently large bacterial population which is capable of utilizing the pollutant as a growth substrate. Frequently, specific organisms with specific enzymes are required to metabolize a pollutant. The processes of species selection and enzyme induction by which a microbial community adapts itself to a pollutant require time. The adaptation time is influenced both by prior exposure of the community to a pollutant and the initial numbers of suitable species. Spain _et al_. (1980) have demonstrated that prior exposure to a compound reduces or eliminates the adaptation period. Thus, lag times in pristine environments should be much longer than in locations which have been chronically exposed to a compound. In addition, Ward and Brock (1976) have shown that lag time preceding the onset of petroleum degradation depends on the initial size of the bacterial population. Water with larger microbial communities should require relatively shorter times to develop a viable population of degraders. High microbial biomass levels are associated with higher BOD_5 concentrations.

The presence of more easily degraded carbon sources may delay the adaptation of a microbial community to the metabolism of a pollutant. Ward and Brock (1976), found that microorganisms in lake water metabolized added glucose completely before degrading hydrocarbons. This diauxic pattern may result in longer lag times.

A final factor which influences lag time is the concentration of the pollutant in the water. There may be concentration thresholds below which adaptation does not take place. (For example, no adaptation for metabolism of 4-nitrophenol occurred at concentrations below about 40 μg/l (Spain *et al*., 1980). Too high a pollutant concentration, on the other hand, may be toxic to the microbes (Tabak *et al*., 1981). The user should be aware of these possibilities when extremely low or high concentrations are involved.

Once the microbial community has adapted to the organic pollutant, it is of interest to know the rate at which biodegradation occurs. Kinetic expressions for compounds used as a growth substrate can be relatively complicated since both the substrate and bacterial concentrations change with time. The Monod equation has been used to describe the degradation rate of a compound which serves as a sole carbon source:

$$-\frac{dC}{dt} = \frac{1}{Y}\cdot\frac{dB}{dt} = \frac{\mu_{max}}{Y}\cdot\frac{B \cdot C}{K_s + C} \qquad \text{(II-56)}$$

where

C = pollutant concentration

B = bacterial concentration

Y = biomass produced per unit C consumed

μ_{max} = maximum specific growth rate

K_s = half-saturation constant

Frequently, the Monod equation is reduced to a second-order biodegradation expression by assuming $C \ll K_s$, in which case:

$$-\frac{dC}{dt} = k_{B2} \cdot B \cdot C \qquad (II-57)$$

where

k_{B2} = second-order biodegradation rate constant
$= \frac{\mu_{max}}{Y \cdot K_s}$

Although Monod kinetics accurately describe some laboratory results, they are inapplicable in the environment due to the presence of other carbon sources. As a simple alternative, first order kinetics are frequently applied:

$$-\frac{dC}{dt} = k_B \cdot C \qquad (II-58)$$

where

k_B = first-order biodegradation rate constant.

This first-order expression is analagous to the equation commonly used for the decay of BOD (see Chapter 4). Larson (1981) has shown that first-order kinetics which include a lag phase (lag time) represent the degradation of growth substrates reasonably well at initial bacterial concentration of 10^6 cells/ml or less, a condition which is usually met in the environment.

2.5.1.2.2 Cometabolism

Microorganisms also degrade compounds which they cannot use as a nutrient or growth substrate through cometabolism. Cometabolism is thought to occur when enzymes of low specificity alter a compound to form products which the other enzymes in the organism cannot utilize. The metabolites formed in the process are structurally similar to their parent molecules and frequently retain their toxicity. In some cases, the product of cometabolism can be used as nutrients by other organisms, but often these intermediate products accumulate (Alexander, 1980).

The kinetics of microbial cometabolism differ significantly from that of growth metabolism. Often no lag occurs before cometabolism begins. The degradation rates, though, are generally slower than the fully adapted rates of growth metabolism (Tiedje, 1980). Since cometabolism does not provide the microbes with any energy, it has no effect on the population size. The rate of cometabolism, however, is directly proportional to the size of the microbial population. Paris _et al_. (1981), showed that a second-order rate law described microbially catalyzed hydrolytic reactions:

$$-\frac{dC}{dt} = k_{B2} \cdot B \cdot C \qquad \text{(II-59)}$$

Since the bacterial population, B, is independent of the rate of cometabolism, it is possible to reduce Equation II-59 to a first-order law by making the following substitution:

$$k_B = k_{B2} \cdot B \qquad \text{(II-60)}$$

In order to use literature values of the second-order biodegradation rate constant in Equation II-60, it is necessary to make an estimate of the size of the bacterial population. Since different techniques of bacterial enumeration can yield results which vary over several orders of magnitude, it is important to use estimates of B based on the same method used to calculate k_{B2}. Table II-21 lists bacterial densities which are typical of lakes and rivers. Obviously, large uncertainties in environmental rates of cometabolism exist due to the wide range of possible bacterial densities. Generally, the user should make conservative assumptions unless other data, e.g. a high BOD, indicate larger bacterial densities.

2.5.1.2.3 Summary

Table II-22 summarizes some of the major differences between growth metabolism and cometabolism. Although the exceptions to the generalizations about each process are numerous and some compounds can undergo both processes, the distinction between the metabolic processes can serve a useful function in a screening method. The generalization about each

TABLE II-21

SIZE OF TYPICAL BACTERIAL
POPULATIONS IN NATURAL WATERS

Water Body Type	Bacterial Numbers (cells/ml)	Ref.
Oligotrophic Lake	50- 300	a
Mesotrophic Lake	450- 1,400	a
Eutrophic Lake	2000-12,000	a
Eutrophic Reservoir	1000-58,000	a
Dystrophic Lake	400- 2,300	a
Lake Surficial Sediments	$8x10^9$ - $5x10^{10}$ cells/g dry wt	a
40 Surface Waters	$500\text{-}1x10^6$	b
Stream Sediments	$10^7\text{-}10^8$ cells/g	c
Rur River (winter)	$3x10^4$	d

References:

[a] Wetzel (1975). Enumeration techniques unclear

[b] Paris et al. (1981). Bacterial enumeration using plate counts.

[c] Herbes & Schwall (1978). Bacterial enumeration using plate counts.

[d] Larson et al. (1981). Bacterial enumeration using plate counts.

TABLE II-22

SUMMARY OF THE CHARACTERISTICS OF THE TWO GENERAL TYPES OF BIODEGRADATION: METABOLISM AND COMETABOLISM (After Tiedje, 1980)

Topics	Metabolism for Growth	Cometabolism*
Distinguishing characteristics	Organism will grow on substance as sole C source. Generally ultimate degradation.	Organism will not grow on substance as sole C source. Accumulation of intermediate products likely.
Degradation rates	High rates.	Generally slow rates.
Behavior at low pollutant concentrations	Possible anamalous behavior due to threshold for enzyme induction.	No anomalous behavior, rates are first order in pollutant concentration.
Acclimation	Major effect: lag may be quite variable or lengthy due to low initial density of degraders, and perhaps starvation state of organisms in natural sample.	Often no effect; rarely causes induction, may increase tolerance to toxic chemical.
Relation of degradation kinetics to total biomass, e.g. decay rate = $k_{B2} \cdot B \cdot C$	Likely not valid, use first-order kinetics.	May be valid since activity of interest is often proportional to general biomass.
Extrapolation	General: expect eventual degradation in nature. Quantitative: difficult to be precise because of growth kinetics and acclimation effects, but may not be important problem because of generally fast rates.	Measure kinetic parameters accurately: because of the generally slower rates, extrapolations will be made over longer times, and thus measured parameters need to be accurate. Also environmental influence factors, e.g. temperature, pH, play a more important role.
Effect of added carbon	Diauxic pattern--more easily metabolized substrates are used first.	Generally effect is proportional to microbial population unless specific carbon source happens to induce or inhibit activity of interest.

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*Alteration of a substrate, for purposes other than growth, e.g. for detoxification process suggest the following approaches when the user has some knowledge of a compound's metabolic pathway:

- Cometabolism -
  - a) Find a second-order rate constant and estimate biomass density. Apply Equations II-59,60.
  - b) When a) is not possible, assume cometabolism is negligible, i.e. $k_B=0$.
- Growth Metabolism
  - a) Find a first- or second-order rate constant.
  - b) Estimate a range of lag times as follows:

For chronically exposed water bodies, assume that no lag time (t_L) occurs. For water bodies not recently exposed (within 200 days) proceed as follows:

1. Estimate lag time using available information. If no information is available use a range of 2-20 days.
2. Assume adaptation occurs as follows:

a) Rivers
- at travel times $< t_L$, $k_B = 0$
- at travel times $\geq t_L$, $k_B \neq 0$

b) Lakes
- for well mixed lakes, first determine C at time $= t_L$, C_{t_L} due to all processes except biodegradation. Then using C_{t_L} as C_o solve for C_t with a modified time, t_m, ($t_m = t - t_L$). (Use equations in Section 5.6.1)
- for stratified lakes use only the volume through which the inflow passes (e.g. the hypolimnion volume) in

calculating the hydraulic residence time (τ_w). Then proceed as above.

c) Estuaries - consider all processes except biodegradation through that downstream segment for which τ_w, as measured from the injection point, becomes greater than t_L. Thereafter include biodegradation.

When no data on which metabolic pathway a compound follows are available, the user should apply any available kinetic information and allow for the possibility of a lag phase prior to the onset of degradation.

2.5.1.3 Chemical Properties Influencing Biodegradation

The chemical properties of a compound determine whether microbes can potentially utilize it as a growth substrate or not. Compounds which serve as bacterial growth substrates usually decay more rapidly than those which microbes cometabolize. Thus, significant differences in the aquatic fate of pollutants can arise depending on which degradation process takes place.

Unfortunately, it is not possible at this time to predict whether a toxic compound is a potential source of energy and carbon solely on the basis of its chemical structure. Rather, the biodegradability of a compound is usually investigated in laboratory tests (Gilbert and Lee, 1980). Compounds which are growth substrates should be able to serve as sole carbon sources for a microbial community. Compounds which cometabolize should degrade only in the presence of another carbon source. A systematic study of the metabolic pathways of the priority pollutants is desperately needed.

Table II-23 contains the results of a preliminary degradation test on the organic priority pollutants (Tabak *et al.*, 1981). Because the experimental conditions were so favorable for biodegradation, the tests serve as a good indicator of a compound's potential biodegradability. Since the pollutants were not the sole carbon sources, no conclusions can be

TABLE II-23

POTENTIAL BIODEGRADABILITY OF ORGANIC POLLUTANTS IN AN AEROBIC ENVIRONMENT
(After Tabak *et al.*, 1981)

Test Compound	Adaptation Summary	Rate Summary	Test Compound	Adaptation Summary	Rate Summary
Pesticides					
Aldrin	N	0	Endrin	N	0
Dieldrin	N	0	Heptachlor	N	0
Chlordane	N	0	Heptachlor epoxide	N	0
DDT p.p'	N	0	Hexachlorocyclohexane α-BHC-alpha	N	0
DDE p.p'	N	0	Hexachlorocyclohexane β-BHC-beta	N	0
DDD p.p'	N	0	Hexachlorocyclohexane ϕ-BHC-delta	N	0
Endosulfan-alpha	N	0	Hexachlorocyclohexane λ-BHC-gamma (lindane)	N	0
Endosulfan-beta	N	0	Acrolein	D	2
Endosulfan sulfate	N	0			
PCB's and Related Compounds					
PCB-1016	N	0	PCB-1248	N	0
PCB-1221	D	2	PCB-1254	N	0
PCB-1232	D	2	PCB-1260	N	0
PCB-1242	N	0	2-Chloronaphthalene	D	2
Halogenated Aliphatic Hydrocarbons					
Chloroethanes			Chloroethylenes		
1,1-Dichloroethane	A	1	1,1-Dichloroethylene	A	2
1,2-Dichloroethane	B	1	1,2-Dichloroethylene-cis	B	1
1,1,1-Trichloroethane	B	1	1,2-Dichloroethylene-trans	B	1
1,1,2-Trichloroethane	C	1	Trichloroethylene	A	1
1,1,2,2-Tetrachloroethane	N	0	Tetrachloroethylene	A	1
Hexachloroethane	D	2	Chloropropanes		
Halomethanes			1,2-Dichloropropane	A	1
Methylene chloride	D	2	Chloropropylenes		
Bromochloromethane	D	2	1,3-Dichloropropylene	A	1
Carbon tetrachloride	D	2	Chlorobutadienes		
Chloroform	A	2	Hexachloro-1,3-butadiene	D	2
Dichlorobromomethane	A	1	Chloropentadienes		
Bromoform	A	1	Hexachlorocyclopentadiene	D	2
Chlorodibromomethane	N	0			
Trichlorofluoromethane	N	0			
Halogenated Ethers					
Bis-(2-chloroethyl) ether	D	2	4-Bromodiphenyl ether	N	0
2-Chloroethyl vinyl ether	D	2	Bis-(2-chloroethoxy) methane	N	0
4-Chlorodiphenyl ether	N	0	Bis-(2-chloroisporopyl) ether	D	2

Results of Tabak *et al.* (1981) using Bunch and Chambers screening test. Results reflect potential biodegradability under favorable conditions. The test measures disappearance rather than mineralization of a compound. A domestic sewage innoculum was used. Test duration = 28 days.

Key to Test Summary

N - Not significantly degraded under conditions of test method.
D - Significant degradation with rapid adaption; < 7 days.
D* - Same as D except slower adaptation at higher pollutant concentration.
A - Significant degradation with gradual adaptation; 7-21 days.
A* - Same as A except no degradation evident at higher pollutant concentration.
B - Slow degradation.
C - Very slow degradation with long adaption period required; >28 days.
T - Significant degradation with gradual adaptation followed by deadaption (toxicity).

Key to Rate Summary

Very crude estimates of first-order biodegradation rate constants may be made from the information given in Tabak *et al.*

0 - No significant degradation rate

1 - $.05\ \text{day}^{-1} < k_B < .5\ \text{day}^{-1}$; use $.05\ \text{day}^{-1}$

2 - $k_B > .5\ \text{day}^{-1}$; use $.5\ \text{day}^{-1}$

TABLE II-23 (continued)

Test Compound	Adaptation Summary	Rate Summary	Test Compound	Adaptation Summary	Rate Summary
Monocyclic Aromatics					
Benzene	D	2	Hexachlorobenzene	N	0
Chlorobenzene	D	2	Nitrobenzene	D	2
1,2-Dichlorobenzene	T	1	Ethylbenzene	D	2
1,3-Dichlorobenzene	T	1	Toluene	D	2
1,4-Dichlorobenzene	T	1	2,4-Dinitrotoluene	T	1
1,2,4-Trichlorobenzene	T	1	2,6-Dinitrotoleune	T	1
Phenolic Compounds					
Phenol	D	2	p-Chloro-m-cresol	D	2
2-Chloro phenol	D	2	2-Nitro phenol	D	2
2,4-Dichloro phenol	D	2	4-Nitro phenol	D	2
2,4,6-Trichloro phenol	D	2	2,4-Dinitro phenol	D	2
Pentachloro phenol	A	1	4,6-Dinitro-o-cresol	N	0
2,4 Dimethylphenol	D	2			
Phthalate Esters					
Dimethyl phthalate	D	2	Bis-(2-ethyl hexyl) phthalate	A	1
Diethyl phthalate	D	2	Di-n-octyl phthalate	A	1
Di-n-butyl phthalate	D	2	Butyl benzyl phthalate	D	2
Polycyclic Aromatic Hydrocarbons					
Napthalene	D	2	Fluorene	A	1
Acenapthene	D	2	Fluoranthene	A*	2
Acenaphthylene	D	2	1,2-Benzanthracene	N	0
Anthracene	A	1	Pyrene	D*	2
Phenanthrene	D	2	Chrysene	A*	1
Nitroso Amines and Miscellaneous Compounds					
Nitrosamines			Substituted benzenes		
N-Nitroso-di-N-propylamine	N	0	Isophorone	D	2
N-Nitrosodiphenylamine	D	2	1,2-Diphenylhydrazine	T	1
			Acrylonitrile	D	2

Results of Tabak et al. (1981) using Bunch and Chambers screening test. Results reflect potential biodegradability under favorable conditions. The test measures disappearance rather than mineralization of a compound. A domestic sewage innoculum was used. Test duration = 28 days.

Key to Test Summary
- N - Not significantly degraded under conditions of test method.
- D - Significant degradation with rapid adaption; < 7 days.
- D* - Same as D except slower adaptation at higher pollutant concentration.
- A - Significant degradation with gradual adaptation; 7-21 days.
- A* - Same as A except no degradation evident at higher pollutant concentration.
- B - Slow degradation.
- C - Very slow degradation with long adaption period required; > 28 days.
- T - Significant degradation with gradual adaptation followed by deadaption (toxicity).

Key to Rate Summary

Very crude estimates of first-order biodegradation rate constants may be made from the information given in Tabak et al.

0 - No significant degradation rate

1 - $.05\ \text{day}^{-1} < k_B < .5\ \text{day}^{-1}$; use $.05\ \text{day}^{-1}$

2 - $k_B > .5\ \text{day}^{-1}$; use $.5\ \text{day}^{-1}$

reached about their metabolic pathways. Some information on the rates of adaptation and decay, though, can be extracted from the results.

The adaptation summary results may be used as follows:

- Rapid Adaptation (D) - Use a range of adaptation times from zero days upward depending upon conditions described above.
- Gradual Adaptation (A) - Use a range of adaptation times from 7 days to more than 20 depending upon the conditions described above.

The rate summary results represent estimates of the biodegradation rate constants assuming the compounds decay according to first-order kinetics. General values presented at the bottom of the table are gross estimates and should only be used if no better data are available. The rate constants should represent an upper limit for biodegradation rates by adapted populations observed in the environment.

Table II-24 contains literature values of biodegradation rate constants. Where possible, the likely metabolic pattern has been indicated. Some of these constants were measured under environmentally relevant conditions. In general, rate constants should be compared with those in Table II-24 before use.

2.5.1.4 Environmental Influences on Biodegradation Rates

Environmental conditions strongly influence the metabolic activity of a microbial community. The environment affects the types of metabolic reactions microbes are able to carry out, the availability of nutrients for these reactions, and the rates at which these reactions occur. The environmental variables which are responsible for these effects are discussed in the following sections.

TABLE II-24

BIODEGRADATION RATE CONSTANTS UNDER AEROBIC CONDITIONS

Compound	k_{B2} Second-Order Rate Constant (ml cell^{-1} day^{-1})	k_B First-Order Rate Constant (1/day)	$t_{1/2}$ Half-Life (days)	T_0 Reference Temperature (°C)	Compound Used as a Growth Substrate?	Experimental Conditions	Ref.
Pesticides							
2,4-D Butoxyethyl ester	$1.2\times10^{-5}{}^{(3}$	$1.3\times10^{-2}{}^{(1}$	53	20	?	Natural surface water samples	a
Malathion	$1.1\times10^{-6}{}^{(3}$	$1.1\times10^{-3}{}^{(1}$	6.3×10^{2}	20	Yes	Natural surface water samples	a
Chlorpropham	$6.2\times10^{-10}{}^{(3}$	$6.2\times10^{-7}{}^{(1}$	1.1×10^{6}	20	?	Natural surface water samples	a
Furadan	2.4×10^{-8}	$2.4\times10^{-5}{}^{(1}$	3×10^{4}	?	?	?	b
Atrazine	2.4×10^{-8}	$2.4\times10^{-5}{}^{(4}$	3×10^{4}	?	?	?	b
Polychlorinated Biphenyls							
Aroclor 1221	-	$.8^{(2}$	.9	?	?	Acclimated activated sludge	c
Aroclor 1016	-	$.2^{(2}$	3.5	?	?	Acclimated activated sludge	c
Aroclor 1242	-	$.15^{(2}$	4.5	?	?	Acclimated activated sludge	c
Aroclor 1254	-	$.1^{(2}$	7.	?	?	Acclimated activated sludge	c
Halogenated Ethers							
4-Chlorophenyl phenyl ether	-	$.011-.016^{(2}$	43-63	?	?	River water; Log = 5-13 days	c
	-	$3.8^{(4}$	.2	?	?	Activated sludge	c
Monocyclic Aromatics							
Nitrobenzene	-	$.7^{(2}$	1.	20	Yes	Adopted activated sludge; COD decay	d
2-Chlorotoluene	$6.5\times10^{-}\ {}^{(3}$	6.5×10^{-4}	1.1x10	?	?	Natural surface water sample	e
Phenolic Compounds							
Phenol	-	$4.^{(2}$	.2	20	Yes	Adapted activated sludge; COD decay	d
	-	$6.^{(2}$	.1	?	?	Polluted river water	c
2-Chlorophenol	-	$1.^{(2}$	.7	20	Yes	Adopted activated sludge	d
	-	.3	2.3	?	?	Soil suspension	c
2,4-Dichlorophenol	-	$.5^{(2}$	1.4	20	Yes	Adapted activated sludge; COD decay	d
	-	$.1^{(4}$	6	25	?	Natural lake waters	c
Pentachlorophenol	-	$.1^{(2}$	7	25	Yes	Unadapted; Nutrient Broth	f
	-	$1.^{(2}$	.7	25	Yes	Adapted; Nutrient Broth	f
2,4-Dimethylphenol	-	$1.^{(2}$	.7	20	Yes	Adapted activated sludge	d
2,4-Dinitrophenol	-	$.2^{(2}$	3.5	20	Yes	Adapted activated sludge	d
2,4,6-Trinitrophenol	-	0		20	No	Activated sludge	d
Phthalate Esters							
Dimethyl	1.2×10^{-4}	$.12^{(1}$	5.6	?	?	?	g
Di-ethyl	7.7×10^{-8}	$7.7\times10^{-5}{}^{(1}$	9.0×10^{3}	?	?	?	g
Di-n-butyl	7.0×10^{-7}	$7.0\times10^{-4}{}^{(1}$	1.0×10^{3}	?	?	?	g
Di-n-octyl	7.4×10^{-9}	$7.4\times10^{-6}{}^{(1}$	9.3×10^{4}	?	?	?	g
Di-(2-ethylhexyl	1.0×10^{-10}	1.0×10^{-7}	6.9×10^{6}	?	?	?	g
	-	$2.5\times10^{-2}{}^{(4}$	28	?	?	River Water	c
Butyl Benzyl	-	$>.35^{(4}$	<2	?	?	River Water	c

TABLE II-24 (continued)

Compound	k_{B2} Second-Order Rate Constant (ml/cell/day)	k_B First-Order Rate Constant (1/day)	$t_{1/2}$ Half-Life (days)	T_o Reference Temperature (°C)	Compound Used as a Growth Substrate?	Experimental Conditons	Ref.
Polycyclic Aromatic Hydrocarbons							
Naphthalene	-	.14	5.0	12	Yes	Contaminated stream sediments	h
	-	$< 4.\times10^{-4}$	1.7×10^{3}	12	?	Pristine stream sediments	h
Anthracene	-	.0025	2.8×10^{2}	12	Yes	Contaminated stream sediments	h
	-	2.5×10^{-4}	2.8×10^{3}	12	?	Pristine stream sediments	h
	-	1.5	.5	?	?	Contaminated stream	c
Benz(a)anthracene	-	$1.\times10^{-4}$	6.9×10^{3}	12	Yes	Contaminated stream sediments	h
	-	$4.\times10^{-6}$	1.7×10^{5}	12	?	Pristine stream sediments	h
Benz(a)pyrene	-	$< 3\times10^{-5}$	large	12	?	Contaminated stream sediments	h
	-	$< 3\times10^{-5}$	large	12	?	Pristine stream sediments	h
Phenanthrene	3.8×10^{-6}	3.8×10^{-3}(1	1.8×10^{2}	?	?	?	e

Notes:

1) First-order rate constant computed using Equation II-60 and $B = 10^3$ cells/ml.

2) First-order constant calculated from percent disappearance and elapsed time.

3) Bacterial enumeration using plate count technique.

4) First-order rate constant computed from reported half-life

References:

a) Paris et al. (1981)

b) Schnoor (1981)

c) Callahan et al. (1979)

d) Pitter (1976)

e) Paris et al. (1980)

f) Kirsch and Etzel (1973)

g) Wolfe et al. (1980)

h) Herbes & Schwall (1978)

2.5.1.4.1 Temperature

In general, a molecule must have an energy greater than a threshold or activation level in order for it to react chemically. Since increasing the temperature increases the number of molecules which have this minimum energy, both biotic and abiotic reactions generally proceed more rapidly at higher temperatures. However, the fact that enzymes catalyze most biochemical reactions, and that microbial populations can adapt to changes in ambient temperatures, complicate the temperature dependence of microbially mediated reactions.

It is common practice to represent the temperature dependence of biodegradation using the following empirical formula:

$$k_B(T) = k_B(T_o) \cdot \Theta_B^{(T-T_o)} \qquad \text{(II-61)}$$

where

$k_B(T)$ = specific biodegradation rate constant at temperature = T
$k_B(T_o)$ = specific biodegradation rate constant at temperature = T_o
T = ambient temperature, °C
T_o = reference temperature, °C
Θ_B = temperature coefficient for biodegradation

The results of Larson et al. (1981) and Ward and Brock (1976) show that the rates of nitrilotriocetate and hydrocarbon biodegradation increased approximately two-fold over a ten degree temperature range ($\Theta_B = 1.072$). Either this value or the typical value of 1.047 used for BOD decay is adequate for screening purposes.

2.5.1.4.2 Nutrient Limitation

Microbes require nutrients such as nitrogen and phosphorus in order to metabolize organic substrates. Several researchers have suggested that inorganic nutrient limitation is a significant factor influencing biodegradation rates in the aquatic environment (Ward and Brock, 1976;

Roubel and Atlas, 1978; Herbes and Schwall, 1978). Ward and Brock (1976) found a high correlation between hydrocarbon degradation rates and phosphorous concentrations in natural waters. The data fit a saturation relationship of the Michaelis-Menten type:

$$k_B(C_p) = k_B(C_p{*}) \cdot \frac{.0277 \cdot C_p}{1 + .0277 \cdot C_p} \qquad \text{(II-62)}$$

where

$k_B(C_p)$ = specific biodegradation rate constant at dissolved inorganic phosphorus concentration, C_p

C_p = dissolved inorganic phosphorous concentration, μg/l

$k_B(C_p{*})$ = non-nutrient limited biodegradation rate onstant

This relationship should serve as a good indicator of possible phosphorous limitation of biodegradation in the environment. Generally surface waters downstream of domestic sewage treatment plants are not limited in either nitrogen or phosphorus. Equation II-62 should be applied only when other nutrients such as carbon and nitrogen are not limiting.

2.5.1.3 Sorption of Substrates

Many organic pollutants adsorb strongly on sediments, (See Section 2.3.2. The difference in the physical and chemical environments between sorbed and dissolved pollutants is likely to influence their availability to microbial organisms. Baughman et al. (1980) showed that the dissolved fraction of the compounds studied was available to biota for degradation while the sorbed fraction was not. In such cases, the rate of disappearance of the pollutant is:

$$\frac{d\,C_T}{dt} = k_B \cdot C_w = \alpha_w \cdot k_B \cdot C_T \qquad \text{(II-63)}$$

where

C_w = the pollutant concentration in the aqueous phase

α_w = the decimal fraction of the total analytical pollutant concentration which is in the aqueous phase (α_w = 1 - fraction sorbed).

It is well known, however, that bacteria grow very readily on surfaces and that increasing available surface area in the form of clays and sediments can increase rates of microbial metabolism. If specific information regarding the effects of sorption on the rates of biodegradation are not available for a compound, it is best to assume that sorption does not change this rate.

2.5.1.4.4 Solubility

Wodzinski and Bertolini (1972) have shown that in the dissolved state, naphthalene and biphenyl were degradable while in the pure crystalline state they were not. Thus, sparingly soluble compounds could degrade slowly for this reason alone. The extent to which this phenomenon applies to other biodegradation reactions has not been established. The user may assume that only dissolved and sorbed chemicals are degraded.

2.5.1.4.5 pH

The hydrogen ion concentration also influences rates of biodegradation. Each bacterial species has a pH range for which it is best suited. Thus, at different pH values, different species may exist, or a given species may metabolize the pollutant at different rates. Hambrick et al. (1980) found that the mineralization rate of naphthalene in oxidizing sediments varied in the proportions 1:6:5 at pH 5, 6.5, and 8. The same study found that the mineralization rates of octadecane varied in the proportions 4:5:7 at the same three pH's. Until more general rules for predicting pH effects are available, the user should assume biodegradation rates are independent of pH in the pH range of 5-9 and decrease outside this range.

2.5.1.4.6 Anoxic Conditions

As the concentration of dissolved oxygen in natural water is depleted, metabolic pathways shift. When the dissolved oxygen concentration drops to about 1 mg/l, the rate of biodegradation becomes dependent on oxygen concentration in addition to substrate concentration and the rate of degradation starts to decrease. At a dissolved oxygen concentration of about 0.5 to 1.0 mg/l, nitrate begins to substitute for molecular oxygen as an oxidant.

When oxygen is depleted anaerobic metabolism prevails with its generally lower energy yields and lower growth rates. Most organic substances are biodegraded more slowly under anaerobic conditions. Rate constants derived for oxygenated systems are no longer appropriate; their use may overpredict the amount of degradation.

Exceptions do exist to the rule of slower degradation under anoxic conditions. Reactions such as dehydrochlorinations and reductive dechlorinations lead to much higher degradation rates for many chlorinated hydrocarbons. Example compounds include lindane, heptachlor, pentachlorophenol, and some one and two carbon chlorinated alkanes.

EXAMPLE II-6

Biodegradability of Naphthalene

Evaluate the biodegradability of naphthalene discharged into the Lepidoptera River by a point source just upstream from Northville's sewage treatment plant. Assume the following water quality parameters at the upstream discharge:

Temperature	= 10°C
Suspended Sediment	= 10 mg/l
Inorganic Phosphorus	= 5 μg/l
Dissolved Oxygen	= 5 mg/l

First, check the potential biodegradability of naphthalene in Table II-23. The table indicates that naphthalene degrades rapidly, $k_B = .5\ \text{day}^{-1}$, and that bacteria adapt quickly to it.

Next, examine Table II-24 for further information on naphthalene's biodegradability. Naphthalene is a potential growth substrate. In addition, the data in this table concur with the rapid degradation rates suggested by Table II-23. In sediment, which had been previously exposed to naphthalene, a biodegradation rate constant of 0.14 day^{-1} was measured. This is close to the rate constant in Table II-24. As one would expect for a growth substrate, degradation rates are much lower, e.g. $k_B < 4\times10^{-4}\ \text{day}^{-1}$, in sites not previously exposed to naphthalene.

Since naphthalene is a growth substrate, estimating the adaptation time in the Lepidoptera River is a primary issue. Because the point source continuously discharges naphthalene into the Lepidoptera River, it is safe to assume that the bacterial populations have adapted.

In a complete analysis, the user would check whether the oxygen is depleted from the river. If so, degradation could be neglected until dissolved oxygen levels exceed 1.0 mg/l again.

Sorption by suspended sediment could potentially reduce the rate at which naphthalene biodegrades. Table II-9 gives a K_{ow} for naphthalene of 2,300. Using Equations II-17 and II-19 and assuming a suspended sediment organic carbon content of 2 percent, the partition coefficient is:

$$K_p = (.02)\ (.63)\ (2{,}300) = 29$$

At the suspended sediment levels in the Lepidoptera River 10 mg/l, Table II-14 shows that sorption will not significantly reduce water column concentrations of naphthalene. Although phosphorus levels are low, assume carbon is the growth-limiting substrate.

Finally, the degradation rate is adjusted to the river water temperature using Equation II-61.

$$k_B = 0.14 \cdot 1.072^{(10-12)} = 0.12\ \text{day}^{-1}$$

END OF EXAMPLE II-6

2.5.2 Photolysis

2.5.2.1 Introduction

The sun provides the aquatic environment with a large supply of energy. Substances which absorb sunlight transform much of its radiant energy into thermal energy. But, molecules which absorb sunlight in the ultraviolet and visible portion of the spectrum may gain sufficient energy to initiate a chemical reaction. Plants use very specific photochemical reactions to provide energy for the synthesis of sugar from carbon dioxide. In other photochemical reactions, the absorption of light leads to the decomposition of a molecule. The latter type of reaction, known as photolysis, strongly influences the fate of certain pollutants in the aquatic environment.

Photolysis is truly a pollutant decay process since it irreversibly alters the reacting molecule. However, the products of the photochemical decomposition of a toxic compound may still be toxic. For example, irradiated 2,4-D esters form 2,4-D acid, a priority pollutant, in aerated waters (Zepp _et_ _al_., 1975). Upon irradiation, DDT reacts to form DDE, which persists in the environment longer than DDT (Tinsley, 1979). Thus, even though the methods in this section assume that pollutants irreversibly decay through photolysis, the planner should remember that the decomposition of a pollutant does not imply the detoxification of the environment.

The rate at which a pollutant photolyzes depends on numerous chemical and environmental factors. The light absorption properties and reactivity of a compound, the light transmission characteristics of natural waters, and the intensity of solar radiation are some of the most important factors influencing environmental photolysis. These factors will be covered by the following discussion. Understanding these factors facilitates the computation of rate constants and the identification of pollutants likely to photolyze - the final two topics of this section.

2.5.2.2 Factors Influencing Photolysis in the Aquatic Environment

2.5.2.2.1 Photochemical Reactions

All chemical reactions which occur at finite rates require the reacting molecule to gain sufficient energy to become "activated" or form a reactive intermediate. In dark or thermal reactions, the thermal energy of the environment supplies the activation energy. In photochemical reactions, the absorption of light provides the activation energy.

The "activated" molecules in photochemical reactions differ in important respects from those of thermal reactions. Thermally activated molecules usually remain in the normal or "ground" electronic energy state, whereas photochemically activated molecules exist in higher, "excited" electronic states. Because of the excess energy and the alteration of the chemical bonds of photoactivated molecules, the range of potential reaction products is much greater than that for thermally activated molecules.

The mechanism by which photoactivated molecules form and react is divided into three steps: 1) the absorption of light to produce an electronically excited molecule, 2) the "primary photochemical processes" which transform or deexcite the excited molecule, and 3) the secondary or "dark" thermal reactions which the intermediates produced in step 2 undergo (Turro, 1978).

The mechanism of photochemical reactions provides a convenient structure for a discussion of the factors which influence photolysis in the aquatic environment. Environmental factors affecting the absorption of light, step 1, will be considered first. Then, the factors influencing the fate of molecules which become excited by the absorption of light, steps 2 and 3, are discussed.

2.5.2.2.2 Light Absorption

> "Only that light which is absorbed by a system can produce chemical changes (Grotthaus-Draper Law)." (Glasstone, 1946)

As this "first law of photochemistry" implies, it is necessary to know the rate at which reacting molecules absorb light in order to determine the rate of a photochemical reaction in the environment. The following factors which influence light absorption in the aquatic environment are discussed here: 1) molecular absorption of light, 2) solar radiation, and 3) light attenuation in natural waters.

2.5.2.2.2.1 Molecular Absorption of Light

Both light and molecules have quantized energies. Light interacts with matter as quanta with energies inversely proportional to their wavelengths. A molecule has quantized internal energy states associated with the configuration of its electrons and the rotation and vibration of its chemical bonds. Since a molecule can absorb light only as a whole photon, light absorption is possible only if the energy of the photon corresponds to the energy change of an allowed transition between the molecule's internal energy states. Consequently, the probability of a photon being absorbed varies strongly with wavelength of the light in a way that is unique to every chemical species.

To initiate a chemical reaction, the absorbed light must be sufficiently energetic to cause a change in the absorbing molecule's electronic structure. Generally, radiation with wavelengths in the ultraviolet-visible range, or shorter, has sufficient energy to initiate photochemical reactions while radiation with wavelengths in the infrared range, or longer, does not. Thus, the ultraviolet-visible light absorption properties of a chemical are of primary interest in photochemistry.

Photochemical reactions in the aquatic environmental depend on the rate at which molecules in aqueous solution absorb light. According to Beer's Law, the rate of light absorption by a single compound (I_a) in a cross-section of solution with infinitesimal thickness (Δz) is proportional to the concentration of the light absorbing species(C), i.e.:

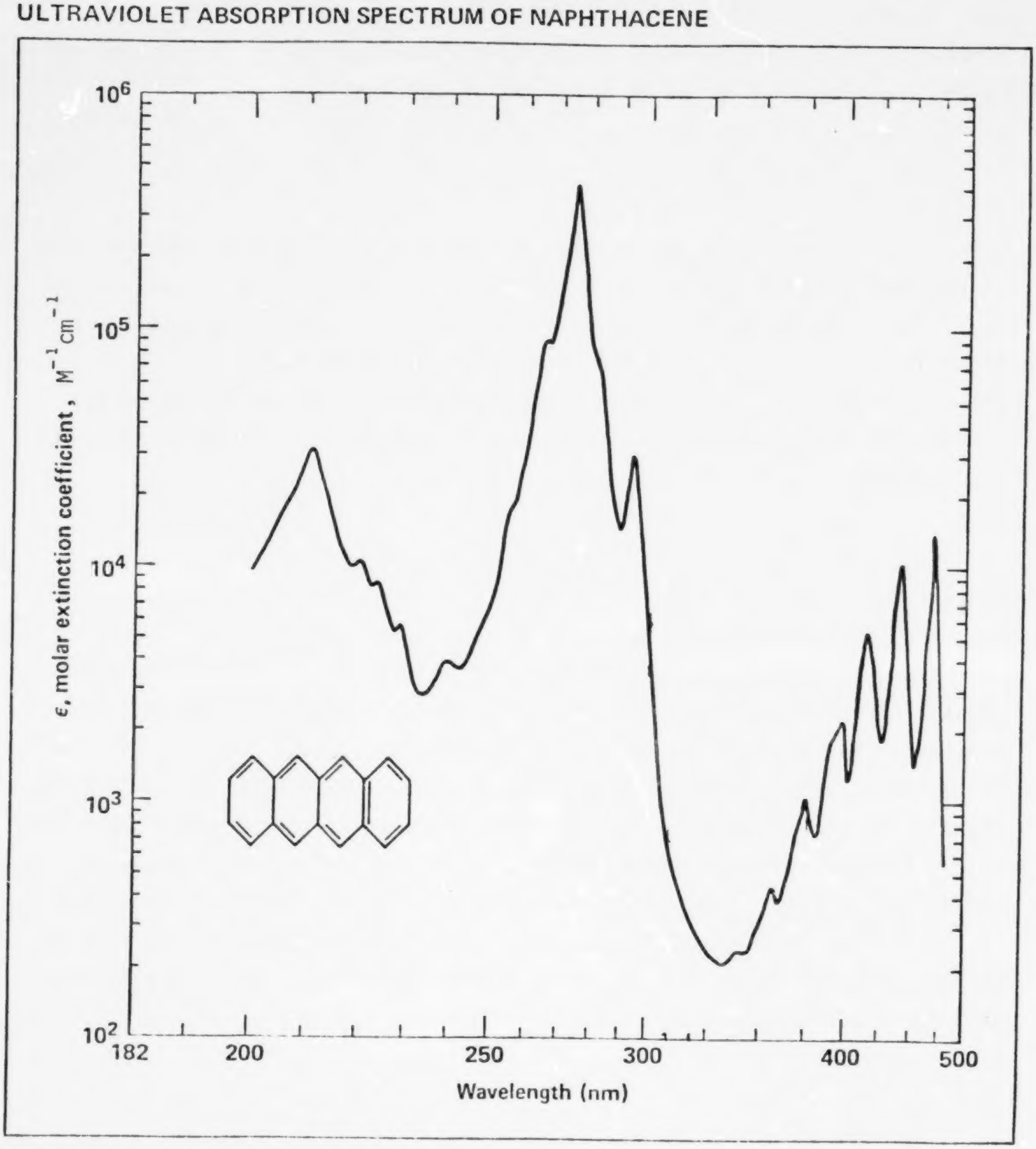
$$I_a(z) = I(z) \cdot 2.3 \cdot \varepsilon \cdot C \cdot \Delta z \qquad \text{(II-64)}$$

where $I(z)$ is the intensity of the light at a depth z in the solution and ε is the base 10 molar extinction coefficient. ε reflects the probability of the light being absorbed by the dissolved molecules and therefore varies with the wavelength of the incident light as shown in Figure II-10. Absorption spectra, such as shown here, contain information necessary to compute the rate at which pollutants absorb radiation available in the environment.

2.5.2.2.2.2 Solar Radiation

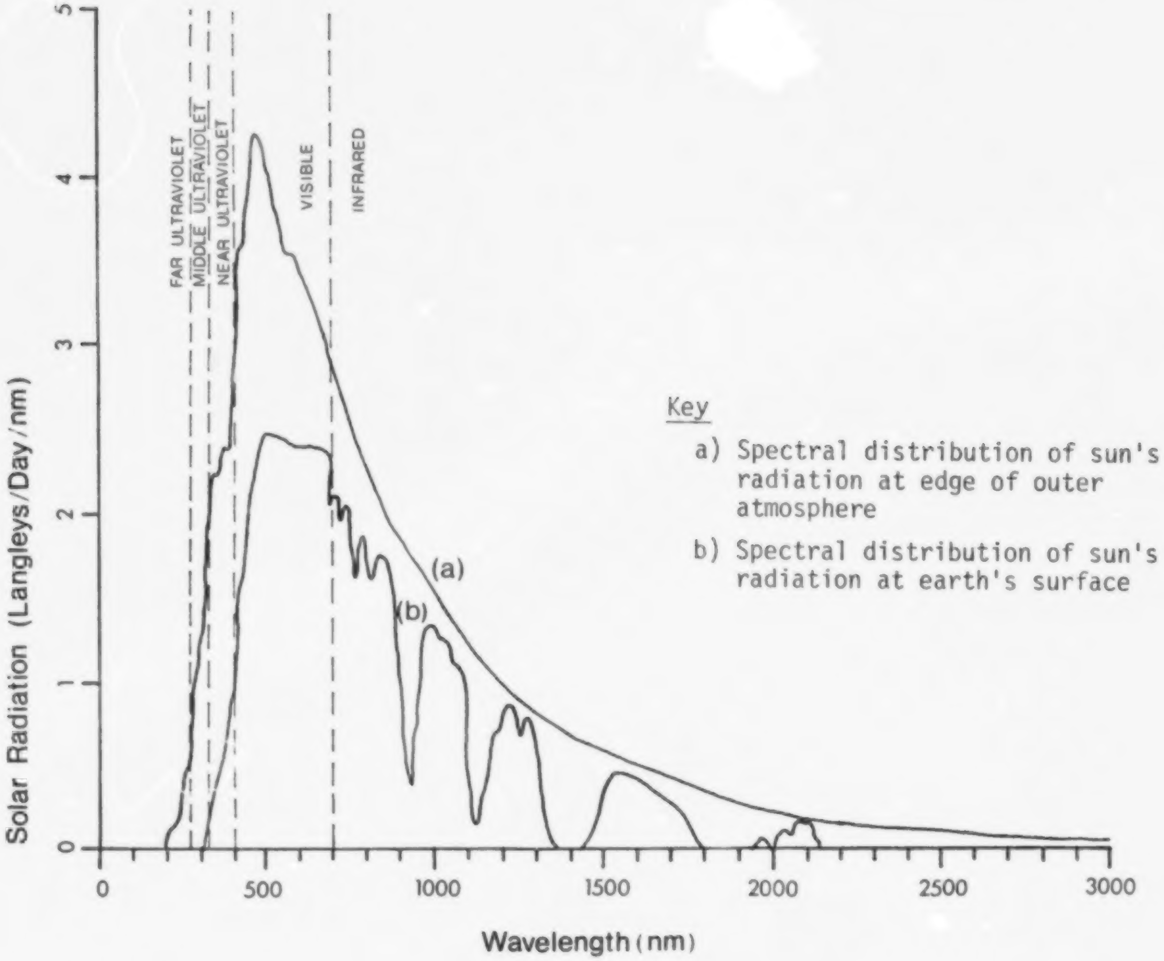
The only radiant energy available for absorption by pollutants in the aquatic environment comes from the sun. The sun emits radiation of nearly constant intensity and spectral distribution. But, gases and particles in the earth's atmosphere alter the incoming solar radiation through scattering and absorption. Scattering of the direct solar beam creates the diffuse or sky radiation visible at the earth's surface. Absorption of both diffuse and direct radiation reduces the intensity of solar radiation reaching the earth. Since the strength of absorption and scattering depends strongly on the wavelength of the light involved, the interaction of sunlight with the atmosphere alters the spectral distribution of solar radiation as well, as Figure II-11 shows.

The composition of the earth's atmosphere and the geometrical relationship of the sun and earth change over time causing the solar radiation incident upon the earth's surface to vary as well. A comparison of the total solar irradiance under clear skies at various times, seasons, and latitudes (Table II-25) to the extra-atmospheric solar flux of 2800 langleys/day demonstrates the effects of changes in earth-sun geometry.



Source: U.V. Atlas of Organic Compounds.

FIGURE II-10 ULTRAVIOLET ABSORPTION SPECTRUM OF NAPHTHACENE



Sources: (a) Weast and Astle (1980); (b) Moon (1940).

FIGURE II-11 SPECTRAL DISTRIBUTION OF SOLAR ENERGY (A) OUTSIDE THE EARTH'S ATMOSPHERE, AND (B) AT THE EARTH'S SURFACE

Table II-25

CALCULATED SOLAR RADIANT ENERGY FLUX TO A HORIZONTAL SURFACE UNDER A CLEAR SKY
(langleys/day)

		Season				
Latitude	Time Of Day	Spring	Summer	Fall	Winter	Annual Mean
30°N	Mean[1]	680	750	530	440	600
	Mid-Day[2]	2100	2200	1700	1400	1900
40°N	Mean	650	740	440	320	540
	Mid-Day	1900	2100	1400	1000	1600
50°N	Mean	590	710	330	190	460
	Mid-Day	1700	1900	1000	650	1300

1) Mean values represent calculated seasonal means under a clear sky. These should represent upper limits for solar radiant energy at sea level. Reference: Weast and Astle (1980).

2) Mid-Day values represent mid-day flux extended over a 24-hour period. These assume an atmospheric turbidity of 0, precipitable water content of 2 cm, and an atmospheric ozone content of .34 cm NTP. Reference: Robinson (1966).

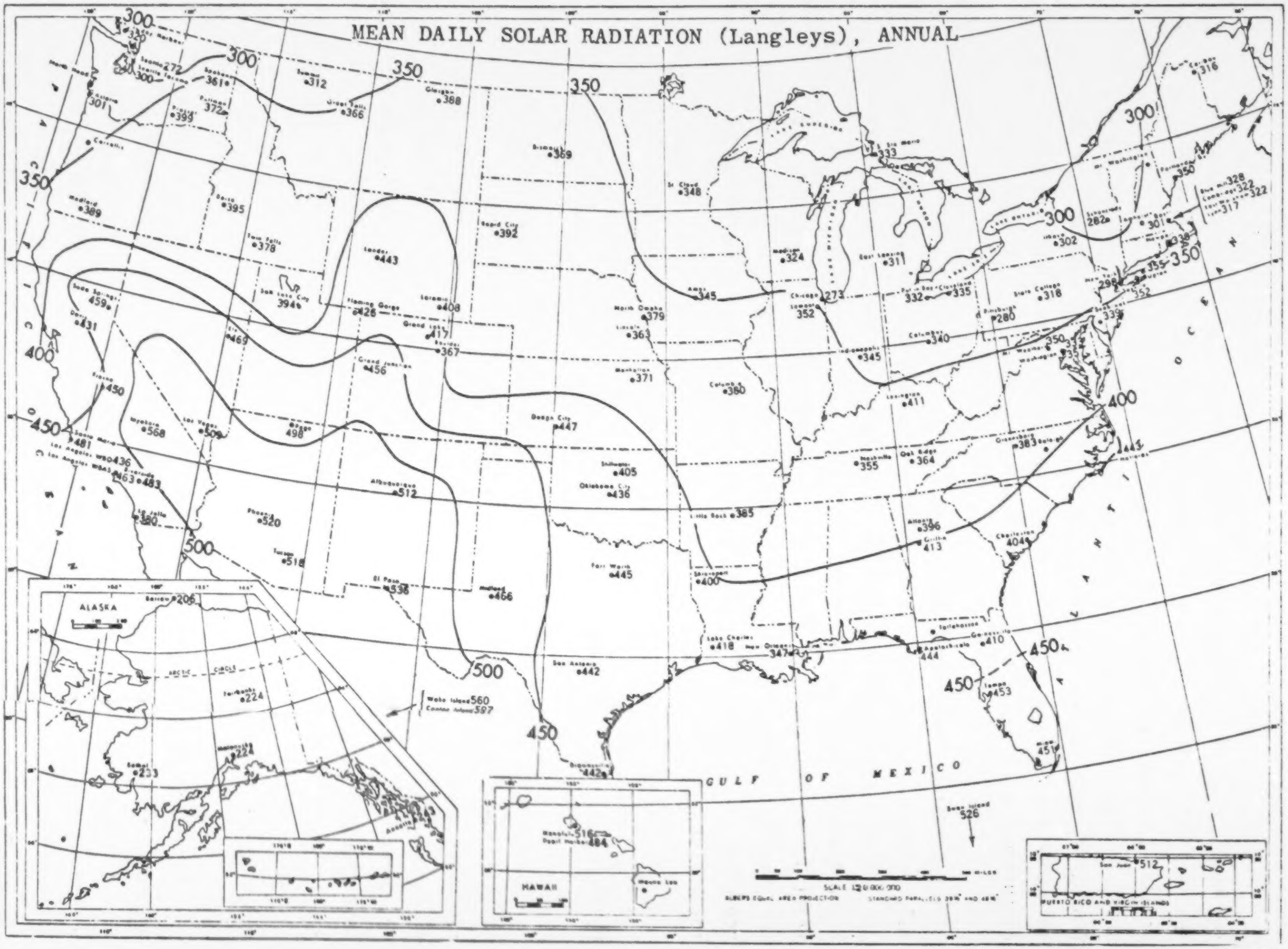
The composition of the atmosphere differs greatly from place to place and is the most difficult of the factors influencing the total solar flux to accurately quantify. Historical records of the solar radiation, such as shown in Figure II-12, are the best way to estimate the mean solar energy flux at a given locale. However, care should be taken to account for the influence of riparian vegetation on incoming radiation. Section 4.4.3 discusses how to approximate the affects of shading.

Information concerning the variability of the spectral distribution of solar energy incident upon the earth's surface is not as readily available. It is known that the fraction of the solar energy in the ultraviolet region decreases with increased attenuation of light by the atmosphere. The fraction of the energy which is visible remains relatively constant. For the purpose of this document, it is sufficiently accurate to assume that the reduction in UV-visible radiation is proportional to the reduction in the total flux.

2.5.2.2.2.3 Light Attenuation in Natural Waters

Just as the earth's atmosphere reduces the intensity of solar radiation reaching the earth's surface, natural waters reduce the intensity of radiation available for absorption by aquatic pollutants. The first process which reduces the availability of light in the water column is reflection. The surface of the water reflects less than 10 percent of solar radiation in most cases (Zepp and Cline, 1977). Reflection also alters the solar spectrum slightly. A calculated spectral distribution of solar radiation, expressed in photons, immediately below the surface of a water body is presented in Table II-26.

As solar radiation penetrates deeper into natural waters, it is absorbed and scattered by particulates, dissolved substances, and water itself. Measurements of light attenuation in natural waters have been based on the decrease of solar irradiance, which includes both collimated and scattered light. Lambert's Law expresses the decrease in the irradiance, I(z), i.e. the total flux incident upon an element of surface divided by its area, with depth, z, as follows:


MEAN DAILY SOLAR RADIATION (Langleys), ANNUAL
300
350
400
450
500
ALASKA
ARCTIC CIRCLE
HAWAII
PUERTO RICO AND VIRGIN ISLANDS
GULF OF MEXICO
Wake Island 560
Canton Island 597
Swan Island 526
Chicago 273
Lemont 352
Madison 324
Ames 345
North Omaha 379
Lincoln 363
Manhattan 371
Columbia 380
Dodge City 447
Stillwater 405
Oklahoma City 436
Little Rock 385
Fort Worth 445
Shreveport 400
San Antonio 442
Brownsville 442
Lake Charles 418
New Orleans 347
Albuquerque 512
Phoenix 520
Tucson 518
El Paso 538
Midland 466
Grand Junction 456
Salt Lake City 394
Ely 469
Las Vegas 509
Inyokern 568
Fresno 450
Davis 431
Santa Maria 481
Los Angeles 436
La Jolla 480
Riverside 483
Medford 389
Boise 395
Twin Falls 378
Lander 443
Laramie 408
Rapid City 392
Bismarck 369
St Cloud 348
Glasgow 388
Great Falls 366
Spokane 361
Seattle 272
Astoria 301
Nashville 355
Oak Ridge 364
Lexington 411
Columbus 340
Indianapolis 345
East Lansing 311
Sault Ste Marie 333
Cleveland 335
Pittsburgh 280
State College 318
Ithaca 302
Atlanta 396
Griffin 413
Charleston 404
Greensboro 383
Apalachicola 444
Gainesville 410
Tampa 453
Miami 451
Barrow 206
Fairbanks 224
Bethel 233
Matanuska 222
Honolulu 516
Pearl Harbor 484
San Juan 512
ALBERS EQUAL AREA PROJECTION
STANDARD PARALLELS 29½° AND 45½°

Ref: US Dept. Comm. (1963)

FIGURE II-12 SOLAR RADIATION IN THE UNITED STATES

Table II-26

CALCULATED SOLAR IRRADIANCE IN A WATER BODY JUST BENEATH THE SURFACE, ANNUAL MEAN AT 40°N

Wavelength[b]	Photon Spectral Irradiance[a]	
	$W(\lambda)$[c]	$W'(\lambda)$[d]
(nm)	(10^{14} photons cm^{-2} $sec^{-1}nm^{-1}$)	(10^{14} photons cm^{-2} $sec^{-1}X$ nm^{-1})
300	.00303	.0303
310	.0388	.388
320	.113	1.13
330	.181	1.81
340	.211	2.11
350	.226	2.26
360	.241	2.41
370	.268	2.68
380	.294	2.94
390	.366	3.66
400	.526	5.26
410	.692	6.92
420	.712	7.12
430	.688	6.88
440	.814	8.14
450	.917	9.17
460	.927	9.27
470	.959	9.59
480	.983	9.83
490	.930	9.30
500	.949	9.49
510	.962	9.62
520	1.00	10.0
550	1.04	52.0
600	1.07	53.5
650	1.08	54.0
700	1.07	53.6
750	1.03	51.5
800	.988	49.4

[a] Estimated reference solar flux, I_o = 540 langleys/day. D_o = 1.0

[b] Centric wavelength of waveband X nm in width, for $300 < \lambda \leq 520$, X=10 nm. For $\lambda \geq 550$, X=50 nm

[c] Mean irradiance over wavelength interval of width X.

[d] Integrated irradiance over wavelength interval of width X. $W'(\lambda)=W(\lambda)\cdot\Delta\lambda=W(\lambda)\cdot X$.

Reference: Burns et al. (1981).

$$-\frac{dI(z)}{dz} = K \cdot I(z) \qquad \text{(II-65)}$$

where K is the diffuse light attenuation coefficient. The diffuse attenuation coefficient can be expressed as a sum of terms accounting for absorption, a, and backward scattering of light, s_b (Smith and Tyler, 1976):

$$K = Da + s_b \qquad \text{(II-66)}$$

where D is the radiance distribution function. Usually, s_b is small compared to the absorption term. The absorption term constitues part of the beam attenuation coefficient, α, which can be measured in a spectrophotometer:

$$\alpha = a + s_b + s_f \qquad \text{(II-67)}$$

where s_f is the forward scattering coefficient of the solution.

The inclusion of the distribution function, D, in Equation (II-66) accounts for the difference in mean light pathlength of collimated and diffuse light. Perfectly diffuse light has a mean path through an element of water which is twice as long as that of a beam of light. The distribution function, generally increases asymptotically with depth due to the increasing fraction of the total light which is scattered. In water bodies where scattering can be ignored, D has a value of 1.2. Miller and Zepp (1979) reported that the mean value of D for six sediment laden waters was 1.6.

The diffuse light attenuation coefficient of natural waters differs greatly due to variations in the types and amounts of particles and dissolved substances in the water. Miller and Zepp (1979), Zepp and Schlotzhauer (1981), and Smith and Baker (1978) have investigated the contributions of suspended sediments, dissolved organic carbon, and chlorophyll pigments to the light attenuation coefficient. By using Equation (II-66) to integrate the results of these investigations, and assuming backscattering to be negligible, Burns et al. (1981) derived the following expression to estimate the diffuse light attenuation coefficient:

$$K = D \cdot \left[a_w + (a_a \cdot \text{chl } \underline{a}) + (a_{DOC} \cdot \text{DOC}) + (a_{ss} \cdot \text{SS})\right] \qquad \text{(II-68)}$$

where a_w = absorptivity of water
a_a = absorptivity of chlorophyll-a pigment
chl a = concentration of chlorophyll-a pigment
a_{DOC} = absorptivity of dissolved organic carbon
DOC = concentration of dissolved organic carbon
a_{ss} = absorptivity of suspended sediments
SS = concentration of suspended sediments

Each absorptivity term varies with the wavelength of light, as shown in Table II-27.

Diffuse light attenuation coefficients can also be estimated using turbidity indicators such as Secchi disc depth. Empirical studies have shown that the diffuse light attenuation coefficient is inversely proportional to the Secchi disc depth, Z_{sd}:

$$K = \frac{R}{Z_{sd}} \qquad \text{(II-69)}$$

The proportionality constant, R, has a value between 1.44 and 1.7 for visible light, i.e. 400-800 nm. In the middle ultraviolet portion of the spectrum, i.e. near 312 nm, R has a value of 9.15 (Zepp, 1980).

2.5.2.2.3 Fate of Excited Molecules

> "Each molecule taking part in a chemical reaction which is a direct result of the absorption of light takes up one quantum of radiation (Stark-Einstein Law)." (Glasstone, 1946)

According to this "second law of photochemistry", the extent to which a photochemical reaction progresses depends on the number of quanta of light absorbed. Each absorbed photon produces an electronically excited molecule which can undergo numerous processes, including reaction. Factors which influence the fraction of excited molecules which undergo reaction, called

Table II-27

CONTRIBUTIONS TO LIGHT ATTENUATION COEFFICIENT

Waveband Center (nm)	a_w [a] (m^{-1})	a_a [b] $[(mg/l)^{-1}\ m^{-1}]$	a_{DOC} [c] $[(mg/l)^{-1}\ m^{-1}]$	a_{ss} [d] $[(mg/l)^{-1}\ m^{-1}]$
300	.141	69.*	6.25	.35
310	.105	67.*	5.41	.35
320	.0844	63.*	4.68	.35
330	.0678	61.*	4.05	.35
340	.0561	58.*	3.50	.35
350	.0463	55.	3.03	.35
360	.0379	55.	2.62	.35
370	.0300	51.	2.26	.35
380	.0220	46.	1.96	.35
390	.0191	42.	1.69	.35
400	.0171	41.	1.47	.35
410	.0162	39.	1.27	.35
420	.0153	38.	1.10	.35
430	.0144	35.	0.949	.35
440	.0145	32.	0.821	.35
450	.0145	31.	0.710	.35
460	.0156	28.	0.614	.35
470	.0156	26.	0.531	.35
480	.0176	24.	0.460	.35
490	.0196	22.	0.398	.35
500	.0257	20.	0.344	.35
510	.0357	18.	0.297	.35
520	.0477	16.	0.257	.35
550	.0638	10.	0.167	.35
600	.244	6.	0.081	.35
650	.349	8.	-	.35
700	.650	3.	-	.35
750	2.47	2.	-	.35
800	2.07	0.	-	.35

Notes:

[a] Source: Smith and Baker (1981)
[b] Source: Smith and Baker (1978) Calculated using $a_a = K_2/D$, D = 1.2
[c] Source: Zepp and Schlotzhauer (1981)
[d] Source: Miller and Zepp (1979). Calculated using $a_{ss} = K_s/D$.

*Denotes extrapolated values.

the quantum yield, comes first in the following discussion of the fate of excited molecules. Then, the two major classes of enviromental photolysis reactions, direct and sensitized, are discussed.

2.5.2.2.3.1 The Quantum Yield

Although all photochemical reactions are initiated by the absorption of a photon, not every absorbed photon induces a chemical reaction. Besides chemical reactions, possible processes which excited molecules may undergo include the reemission of light through flourescence and phosphorescence, the internal conversion of the photons' energy into heat, and the excitation of other molecules, as shown in Figure II-13. The fraction of absorbed photons which cause the desired reaction(s) is termed the quantum yield, ϕ:

$$\phi \equiv \frac{\text{moles of a given species formed or destroyed}}{\text{moles of photons absorbed by the system}} \qquad \text{(II-70)}$$

The quantum yields for photochemical reactions in the solution phase exhibit two properties which greatly simplify their use:

- The quantum yield is less than or equal to one.
- The quantum yield is independent of the wavelength of the absorbed photons.

Although exceptions to these rules exist, they are rare for photochemical reactions in the aquatic environment.

Environmental conditions influence photolysis quantum yields. Molecular oxygen acts as a quenching agent (see Figure II-13) in some photochemical reactions, reducing the quantum yields (Wolfe *et al*., 1978). In other cases, it has no effect or may even be a reactant. In any case, rate constant and quantum yield measurements should be performed in water with oxygen concentrations representative of environmental conditions.

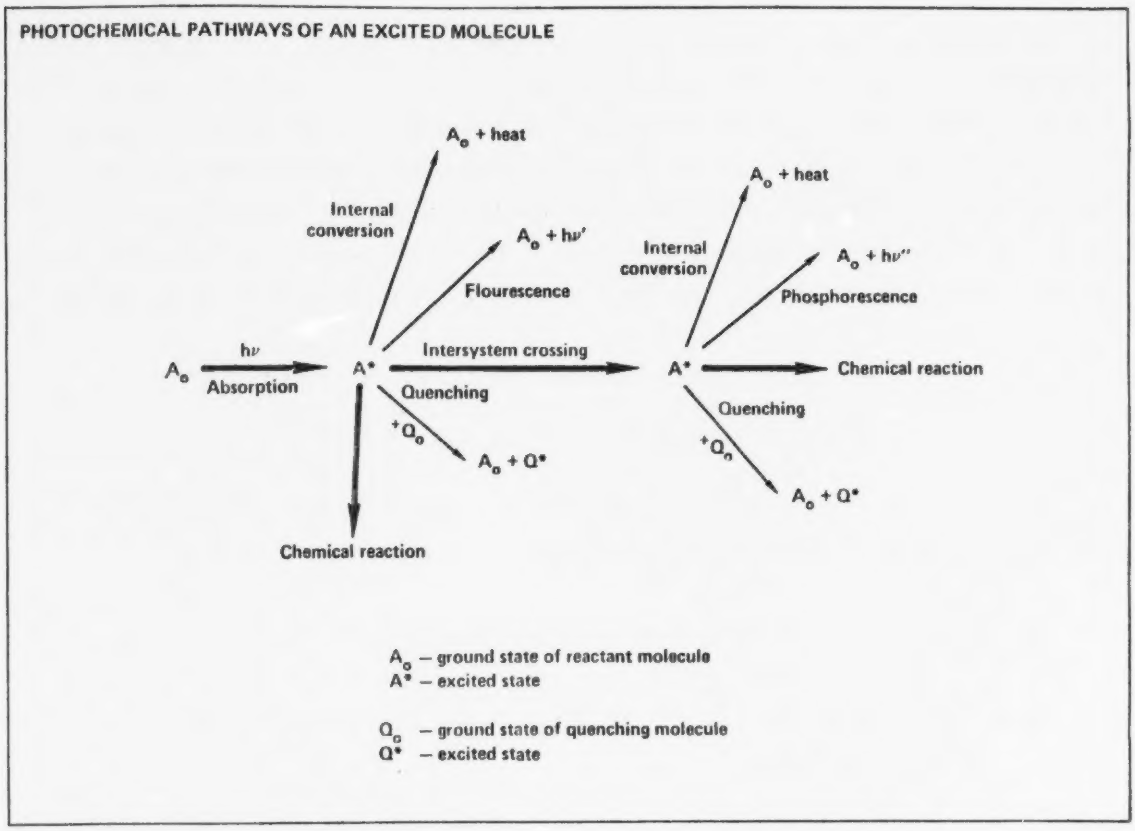

PHOTOCHEMICAL PATHWAYS OF AN EXCITED MOLECULE
A_o + heat
Internal conversion
A_o + $h\nu'$
Flourescence
A_o
$h\nu$
Absorption
A^*
Intersystem crossing
Quenching
^+Q_o
$A_o + Q^*$
Chemical reaction
A_o + heat
Internal conversion
A_o + $h\nu''$
Phosphorescence
A^*
Chemical reaction
Quenching
^+Q_o
$A_o + Q^*$
A_o – ground state of reactant molecule
A^* – excited state
Q_o – ground state of quenching molecule
Q^* – excited state

Figure II-13 Photochemical Pathways of an Excited Molecule. Excited molecules do not always chemically react.

Suspended sediments also influence rates of photolysis. Not only do suspended sediments increase light attenuation, but they change the reactivity of compounds sorbed on them (Miller and Zepp, 1979). Sorption may either increase or decrease a compound's reactivity depending on the reaction it undergoes. This effect, however, is of secondary importance in comparison to the increase in light attenuation by the suspended sediments (Burns et al., 1981). Thus, the effects of sorption will be neglected.

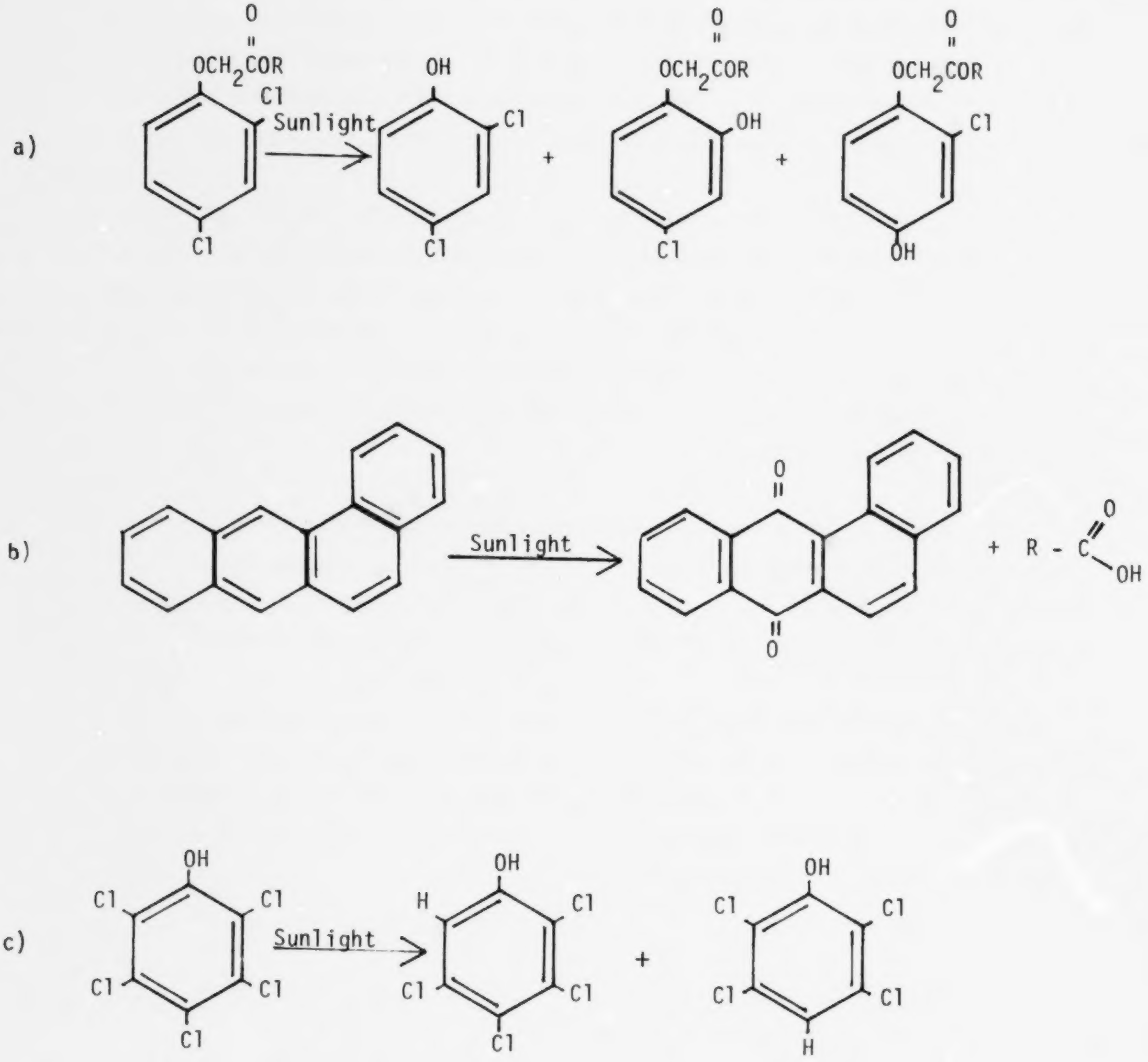
Chemical speciation also effects rates of photolysis. Different forms of an organic acid or base may have different quantum yields, as well as absorptivities, causing the apparent photolysis rate of the compound to vary with pH. The possibility of this should be kept in mind when the pK_a of a photolyzing compound is 7 ± 2. Except where stated otherwise, data contained herein may be assumed independent of pH over the range of values observed in natural waters.

Photochemicaly initiated reactions may show a temperature effect depending upon the actual mechanisms involved. General methods for predicting this effect have yet to be developed. Users of this screening manual should assume thermal effects on photolysis to be negligible.

Quantum yields vary over several orders of magnitude depending on the nature of the molecule which absorbs light and the nature of the reactions it undergoes. The two major classes of photochemical reactions of interest in the aquatic environment are direct and sensitized photolysis. A closer examination of each reaction type follows.

2.5.2.2.3.2 Direct Photolysis

Direct photolysis occurs when the reacting molecule itself directly absorbs light. The excited molecule can undergo various types of reactions, including fragmentation, reduction, oxidation, hydrolysis, acid-base reaction, addition, substitution, isomerization, polymerization, etc. Figure II-14 shows examples of the reactions undergone by three toxic substances which directly photolyze.



a)
O
OCH2COR
Cl
Sunlight
Cl
OH
Cl
Cl
+
O
OCH2COR
OH
Cl
+
O
OCH2COR
Cl
OH
b)
Sunlight
O
O
+ R - C
O
OH
c)
OH
Cl
Cl
Cl
Cl
Cl
Sunlight
OH
H
Cl
Cl
Cl
Cl
+
OH
Cl
Cl
Cl
Cl
H

FIGURE II-14 DIRECT PHOTOCHEMICAL REACTIONS OF (A) 2,4-D ESTER, (B) BENZ(A)ANTHRACENE, AND (C) PENTACHLOROPHENOL.

The quantum yield for the direct photolysis, ϕ_d, of a compound is a constant defined as follows:

$$\phi_d = \frac{-dC}{dt} \Big/ I_{ad} \qquad \text{(II-71)}$$

where C is the concentration of the compound and I_{ad} is the rate at which the compound absorbs light. Table II-28 lists several disappearance quantum yields for direct photolysis of aquatic pollutants.

By comparing molecular absorption spectra with the spectral distribution of sunlight, it is possible to determine whether or not a compound may directly photolyze. Benzene, as shown in Figure II-15a, does not directly photolyze because it does not absorb light above 275 nm. Naphthacene, shown in Figure II-15b, does directly photolyze because of its strong absorptivity in the sunlight region of the spectrum. Humic acids, Figure II-15c, by virtue of their absorption of sunlight may initiate indirect, or sensitized, photochemical reactions.

2.5.2.2.3.3 Sensitized Photolysis

Sunlight can cause the degradation of aquatic pollutants by means other than direct photolysis. A light-absorbing molecule can transfer its excess energy to an acceptor molecule causing the acceptor to react as if it had absorbed the radiant energy directly. This reaction mechanism, known as photosensitization, contributes to the degradation of aquatic pollutants when suitable light absorbing substances, or photosensitizers, are present. 2,5-Dimethylfuran is an example of a compound which degrades by sensitized photolysis. It does not react when exposed to sunlight in distilled water but degrades rapidly in waters containing natural humic acids (Zepp et al., 1981a).

Numerous substances, including humic acids, titanium dioxide, and synthetic organic compounds, can sensitize photochemical reactions. But, most potential sensitizers occur at such low environmental concentrations that they have negligible effects on photolysis rates. Humic acids, the naturally occurring by-products of plant matter decay, frequently attain

Table II-28

DISAPPEARANCE QUANTUM YIELDS, ϕ_d FOR DIRECT PHOTOLYSIS

Compound		ϕ_d	Reference
Polycyclic Aromatic Hydrocarbons			
Naphthalene		.015	a
1-Methylnaphthalene		.018	a
2-Methylnaphthalene		.0053	a
Phenanthrene		.010	a
Anthracene		.0030	a
9-Methylanthracene		.0075	a
9,10-Dimethylanthracene		.0040	a
Pyrene		.0021	a
Fluoranthrene	(313 nm)	.00012	a
	(366 nm)	.000002	a
Chrysene		.0028	a
Naphthacene		.013	a
Benz(a)anthracene		.0033	a
Benz(a)pyrene		.00089	a
2,4-D Esters			
Butoxyethyl ester		.056	b
Methyl ester		.031	b
Carbaryl		.0055	c
N-Nitrosoatrazine		.30	d
Trifluralin		.0020	d
DMDE		.30	d

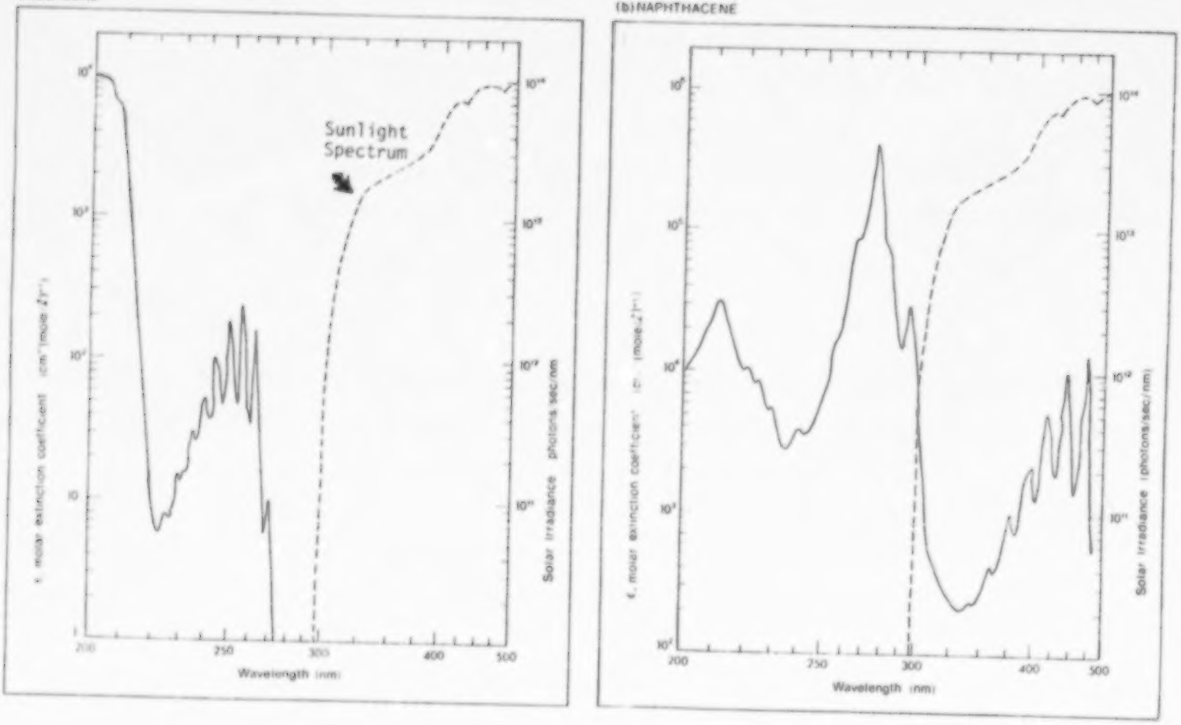
References:

[a] Zepp and Schlotzhauer (1979)

[b] Zepp *et al*. (1975)

[c] Wolfe *et al*. (1978)

[d] Zepp and Cline (1977)



(a) BENZENE

(b) NAPHTHACENE

(c) HUMIC ACID

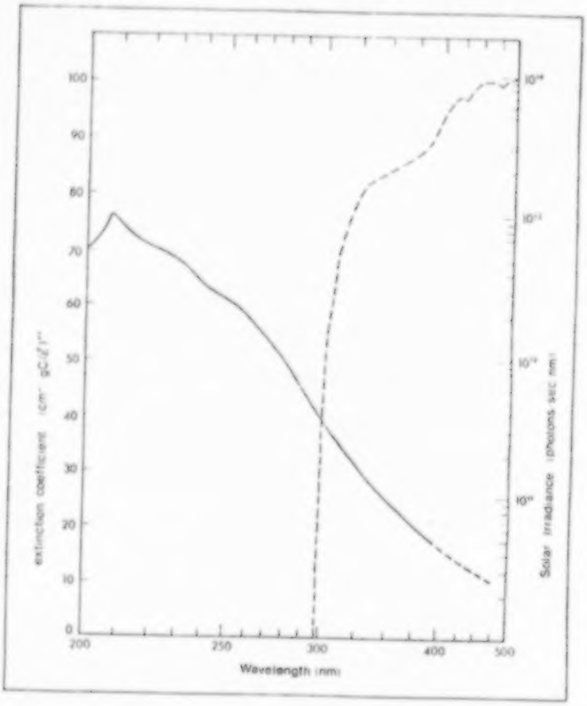


FIGURE II-15

COMPARISON OF SOLAR IRRADIANCE WITH THE ABSORPTION SPECTRA OF (A) A COMPOUND WHICH DOES NOT DIRECTLY PHOTOLYZE, (B) A COMPOUND WHICH DOES DIRECTLY PHOTOLYZE, AND (C) A SUBSTANCE WHICH INITIATES INDIRECT PHOTOCHEMICAL REACTIONS

References: Sunlight spectrum, Burns *et al.* (1981); Benzene and naphthacene spectra, *U.V. Atlas of Organic Compounds*; Humic acid spectrum, Schnitzer (1971).

concentrations of 1-10 mg as carbon per liter in natural systems. Humic acids strongly absorb sunlight with wavelengths shorter than 500 nm, as the absorption coefficients for dissolved organic carbon, a_{DOC}, in Table II-27 indicate.

The quantum yield for photosensitized reactions, ϕ_s, is defined in a manner similar to the quantum yield for direct photolysis:

$$\phi_s = \frac{-dC}{dt} \Big/ I_{as} \qquad \text{(II-72)}$$

where C is the concentration of the pollutant and I_{as} is the rate of light absorption by the sensitizing molecule. The quantum yield for sensitized photolysis, however, is not constant but depends on the pollutant concentration, such that:

$$\phi_s = Q_s \cdot C \qquad \text{(II-73)}$$

where Q_s is a constant. This is due to the fact that the probability of the sensitized molecule donating its energy to a pollutant molecule is proportional to the concentration of the pollutant molecule. Published values of Q are very rare. Zepp et al. (1981b) report a Q of 19 $(mol/l)^{-1}$ for the photosensitized ozidation of 2,5-dimethylfuran.

2.5.2.3 Computing Environmental Photolysis Rates

The overall rate at which a pollutant photolyzes in the aquatic environment is the sum of the rates of direct and sensitized photochemical reactions. At the low pollutant concentrations observed in the environment, the rates of both direct and sensitized photolysis are proportional to the concentration of the pollutant. Thus, photolysis follows a first-order rate law:

$$\frac{dC}{dt} = -k_p \cdot C \qquad \text{(II-74)}$$

where

k_p = overall photolysis rate constant, day^{-1}

$= k_d + k_s$

k_d = direct photolysis rate constant, day^{-1}

k_s = sensitized photolysis rate constant, day^{-1}

Due to the complexity of the units for the parameters in the photolysis section, it is essential that the user employ the specified units in each equation. All resulting first-order photolysis rate constants have units of day^{-1}.

The determination of rate constants for direct and sensitized photolysis is the subject of the remainder of this section. Section 2.5.2.3.1 includes a derivation of the equations for k_d and k_s. Sections 2.5.2.3.2 and 2.5.2.3.3 describe how to calculate these constants on the basis of near surface rate constants or molecular absorption spectra.

2.5.2.3.1 Derivation of Rate Constant Equations

2.5.2.3.1.1 Direct Photolysis

The rate at which a compound directly photolyzes is proportional to the rate at which it absorbs light. The rate of light absorption by a dissolved substance in natural waters is (Miller & Zepp, 1979):

$$I_{ad} = \frac{1}{Z}\int_{0}^{Z}\int_{\lambda_0}^{\lambda_1} 2.3\cdot j\cdot \varepsilon(\lambda)\cdot C(z)\cdot D(z)\cdot W(\lambda)\cdot e^{-K(\lambda)\cdot z}\, d\lambda dz \qquad \text{(II-75)}$$

where

I_{ad} = rate of light absorption, einstein l^{-1} day^{-1}

Z = mixed depth of water body, m

λ_1 = 500 nm

$\lambda_o \approx$ 300 nm

j = conversion factor = 1.43×10^{-16} mole$\cdot$cm$^3\cdot$sec$\cdot$l$^{-1}\cdot$day^{-1}

ε = base 10 molar extinction coefficient of pollutant, l mol^{-1} cm^{-1}

C = concentration of pollutant, mol/l

D = radiance distribution function

W = photon irradiance near the surface, photons cm^{-2} sec^{-1} nm^{-1}

K = diffuse light attenuation coefficient of the water, m^{-1}

The expression for the direct photolysis rate constant, which can be derived from Equations (II-71), (II-74), and (II-75) is:

$$k_d = 2.3 \cdot j \cdot \phi_d \cdot D \cdot \int_{\lambda_o}^{\lambda} \varepsilon \cdot W \cdot \frac{1-e^{-K \cdot Z}}{K \cdot Z} \cdot d\lambda \qquad \text{(II-76)}$$

Equation (II-76) incorporates the assumption that C, K, and D are independent of depth. Thus, it will overpredict photolysis rates if the pollutant is not distributed evenly throughout the water column.

2.5.2.3.1.2 Sensitized Photolysis

The rate at which a compound decays through sensitized photolysis is proportional to the rate at which sensitizing molecules absorb light. The rate at which sensitizers absorb light in the aquatic environment is:

$$I_{as} = \frac{1}{Z} \int_{0}^{Z} \int_{\lambda_0}^{\lambda_1} j \cdot a_s(\lambda) \cdot C_s(z) \cdot D(z) \cdot W(\lambda) \cdot e^{-K(\lambda)z} \, d\lambda dz \qquad \text{(II-77)}$$

where

I_{as} = rate of light absorption by sensitizers, einstein $l^{-1}day^{-1}$

a_s = base e absorption coefficient of the sensitizer, e.g. l $mg\text{-}DOC^{-1}$ cm^{-1}

C_s = concentration of sensitizer, e.g. mg-DOC/l

The rate constant for sensitized photolysis of a compound, k_s, is then:

$$k_s = j \cdot C_s \cdot D \cdot Q_s \cdot \int_{\lambda_0}^{\lambda_1} a_s \cdot W \cdot \frac{1 - e^{-K Z}}{K \cdot Z} \cdot d\lambda \qquad \text{(II-78)}$$

Equation (II-78) includes the assumptions that C_s, K, and D are independent of depth and that Q_s is independent of wavelength

2.5.2.3.2 Use of Near Surface Rate Constants

Experimental data for direct photolysis are generally reported as near surface rate constants, as in Table II-29. Near the surface of a water body ($K \cdot z \leq 0.2$), the mean irradiance is approximately equal to the surface irradiance. This fact permits Equation (II-76) to be simplified to the following expression which defines the near surface rate constant, k_{do}:

Table II-29

NEAR-SURFACE DIRECT PHOTOLYSIS RATE CONSTANTS

Compound[1]	k_{do} [1] (day^{-1})	I_o [2] (langleys/day)	λ^* [3] (nm)	Ref.
Polycyclic Aromatic Hydrocarbons	9			
Naphthalene	.23	2100	310	a
1-Methylnaphthalene	.76	2100	312	a
2-Methylnaphthalene	.31	2100	320	a
Phenanthrene	2.0	2100	323	a
Anthracene	22.0	2100	360	a
9-Methylanthracene	130.0	2100	380	a
9,10-Dimethylanthracene	48.0	2100	400	a
Pyrene	24.0	2100	330	a
Fluoranthrene	.79	2100	-	a
Chrysene	3.8	2100	320	a
Naphthacene	490.0	2100	440	a
Benzo(a)pyrene	31.0	2100	380	a
Benzo(a)anthracene	28.0	2100	340	a
Carbamate Pesticides				
Carbaryl	.32	2100	313	b
Propham	<.003	740	-	c
Chlorpropham	<.006	740	-	c
Phthlate Esters				
dimethyl ester	5×10^{-3}	600	-	d
diethyl ester	5×10^{-3}	600	-	d
di-n-butyl ester	5×10^{-3}	600	-	d
di-n-octyl ester	5×10^{-3}	600	-	d
di-(2-ethylhexyl) ester	5×10^{-3}	600	-	d
2,4-D Esters				
butoxyethyl ester	.050	420	-	e
methyl ester	.030	420	-	e
Hexachlorocyclopentadiene	94.	540	-	f
Pentachlorophenol (anion)	.46	600	318*	f
3,3'-dichlorobenzidine	670.	2000	280-330*	f
N-nitrosoatrazine	300.	1800	-	g
Trifluralin	30.	1800	-	g
DMDE(1,1-bis(p-methylphenyl 1)-2,2-dichloroethylene)	17.	2200	-	g

Notes:

1) Parenthetic comments after name of compound indicate when the form of the compound undergoing photolysis is something other than the neutral form.

2) Estimated Solar Flux - usually high estimates to give conservative photolysis rates.

3) Wavelength of maximum sunlight absorption.

* Indicates the maximum of the absorption spectrum is used.

References:

a) Zepp and Schlotzhauer (1979)
b) Zepp (1978)
c) Wolfe *et al*. (1978)
d) Wolfe *et al*. (1980)
e) Zepp *et al*. (1979)
f) Callahan *et al*. (1979)
g) Zepp and Cline (1977)

$$k_{do} = 2.3 \cdot \phi_d \cdot D_o \cdot j \cdot \int_{\lambda_o}^{\lambda_1} \varepsilon \cdot W \cdot d\lambda \qquad \text{(II-79)}$$

where

k_{do} = near-surface direct photolysis rate constant, day^{-1}

D_o = radiance distribution near the surface (approximate value = 1.2)

According to Equation (II-79), the near surface rate constant is independent of the properties of the water it is measured in, except for the small variation in D_o. Thus, when the difference in solar irradiance between the experimental and environmental conditions is accounted for, the user can apply a near surface rate constant to other bodies of water using the following expression:

$$k_d = k_{do} \cdot \frac{I}{I_o} \cdot \frac{D}{D_o} \cdot \frac{1-e^{-K(\lambda^*) \cdot Z}}{K(\lambda^*) \cdot Z} \qquad \text{(II-80)}$$

where

I = total solar radiation (langleys/day)

I_o = total solar radiation under conditions at which k_{do} was measured (langleys/day)

λ^* = wavelength of maximum light absorption, i.e. wavelength where the product $\varepsilon(\lambda) \cdot w(\lambda)$ is greatest.

This approximate expression is valid if the following assumptions are sufficiently accurate: 1) the solar irradiance at a wavelength is a constant fraction of the total solar irradiance (Park *et al*., 1980) and 2) the light attenuation coefficient, K, is constant over the range of wavelength that the compound absorbs solar radiation at high rates (Burns *et al*., 1981).

Although it is possible to derive a similar expression for sensitized photolysis, variation in the absorptivity and reactivity of natural humic substances make extrapolations based on the concentration of dissolved organic carbon subject to large errors. An approach taken by Zepp (1980) was to correlate the sensitized photolysis rate constant with the absorbance of a solution at 366nm. Such an empirical relationship was found for 2,5-dimethylfuran:

$$\log k_{so} = .67 \log a_{366} - 1.15 \qquad \text{(II-81)}$$

where

a_{366} = absorbance of solution at 366nm

k_{so} = near surface rate constant, $\text{day}^{-1}\,\text{cm}^{-1}$ (I_o=1 langley/day).

At present, data on sensitized photolysis are difficult to obtain. The planner should be aware of its potential significance even if it is not possible to estimate rates at this time.

2.5.2.3.3 Evaluation of Rate Constant Integrals

When both the absorption spectrum, $\varepsilon(\lambda)$ or $a_s(\lambda)$, and the quantum yields, ϕ_d or Q_s, are available, it is possible to evaluate the integrals in Equations II-76 and II-78 numerically, as shown below:

$$k_d = 2.3 \cdot j \cdot \phi_d \cdot D \cdot \sum_i \varepsilon \cdot W' \cdot \frac{1-e^{-K \cdot Z}}{K \cdot Z} \qquad \text{(II-82)}$$

$$k_s = j \cdot Q_s \cdot D \cdot C_s \cdot \sum_i a_s \cdot W' \cdot \frac{1-e^{-K \cdot Z}}{K \cdot Z} \qquad \text{(II-83)}$$

where

i = index of wavelength interval

$W' = W \cdot \Delta\lambda$

The user may obtain information necessary to evauate these expressions from the following sources:

- W' - Table II-26.
- K - Equation (II-68) and Table II-27 or Equation (II-69).
- D - Assign a value between 1.2 and 2 as follows: 1.2 for very clear waters, 1.6 for typical rivers, 2 for extremely turbid waters.
- ε - Spectroscopy reference works, e.g. Stadler U.V. Spectra or U.V. Atlas of Organic Compounds.
- ϕ_d - Literature or Table II-28.
- a_s - For reactions sensitized by humic acids, use a_{DOC} in Table II-27.
- Q_s - Literature (rarely available).

EXAMPLE II-7

Computation of Photolysis Rate Constants

Compute the mean annual photolysis rate constant for the pesticide carbaryl in a hypothetical river near Fresno, California. Use both the evaluation of integral and near surface rate constant methods described above. Assume the following physical and chemical parameters apply to the river:

Mean Depth = 2 m
Suspended Sediments - 10 mg/l
Humic Acid = 2 mg-DOC/l
Chlorophyll a = 0 mg/l

Zepp (1978) reported a quantum yield, ϕ_d, of .0060 and the following absorptivities, ε, for carbaryl:

Wavelength (nm)	Absorptivity (M^{-1} cm^{-1})
300	918
310	356
320	101
330	11

A. Near Surface Rate Constant Method

Table II-29 contains the following information regarding carbaryl:

$$k_d = .32 \text{ day}^{-1}$$
$$I_o = 2100 \text{ langleys/day}$$
$$\lambda^* = 313 \text{ nm}$$

According to Figure II-12, the mean annual solar irradiance at Fresno, California is 450 langleys/day.

Assume that the radiance distribution function under reference, D_o, and environmental, D, conditions have values of 1.2 and 1.6 respectively.

To calculate the light attenuation coefficient at the wavelength of maximum light absorption, 313 nm, we use Equation (II-68) and the data in Table II-27, at 310 nm;

$$K = 1.6\ (.105 + 67\cdot 0 + 5.41 \cdot 2 + .35 \cdot 10) = 23.1 m^{-1}$$

When the water absorbs nearly all of the incident radiation, i.e. $kZ \geq 3$, the following approximation is valid:

$$\frac{1 - e^{-KZ}}{KZ} \approx \frac{1}{KZ}$$

This approximation can be applied to Equation (II-80) and Equation (II-82). It both simplifies the calculations and eliminates the dependence of the rate constant on the radiance distribution function, D, in cases where the light attenuation coefficient is calculated from D, as in this example. In such a case, the user's choice of a value of D does not affect the result.

Using this approximation in Equation (II-80), the mean photolysis rate constant is computed to be:

$$k_d = .32\ \text{day}^{-1} \cdot \frac{450}{2100} \cdot \frac{1.6}{1.2} \cdot \frac{1}{23.1 \cdot 2}$$

$$= 2.0 \times 10^{-3}\ \text{day}^{-1}$$

This example demonstrates the significant difference, 100 fold in this case, which may exist between near surface and mean photolysis rate constants. The strong attenuation of light by the river water was the primary cause of the reduction in rates.

B. Evaluation of Integrals

The absorption data for carbaryl indicate that we need to concern ourselves only with light of wavelength 300-330 nm in order to determine a mean rate constant.

First, we assume that D has the same value as above, 1.6. Then, we compute the light attenuation coefficients using Equation (II-68) and the data in Table II-27.

λ (nm)	$D \cdot$	$[a_w$ (m^{-1}) $+$	$(a_{DOC}$ [(mg/l)$^{-1}$m^{-1}] $\cdot$	$C_{DOC})$ (mg/l) $+$	$(a_{ss}$ [(mg/l)$^{-1}$m^{-1}] $\cdot$	$C_{ss})]$ (mg/l) $=$	K (m^{-1})
300	1.6	.141	6.25	2	.35	10	25.8
310	1.6	.105	5.41	2	.35	10	23.1
320	1.6	.0844	4.68	2	.35	10	20.7
330	1.6	.0678	4.05	2	.35	10	18.7

Table II-26 lists the photon spectral irradiance, W', at a reference total sloar flux, I_o, of 540 langleys/day. The local solar flux, as in part A, is 450 langleys/day.

Next, evaluate the sum indicated in Equation (II-82).

Since KZ >3 for all wavelengths of interest, use the approximation discussed in part A.

λ (nm)	ε ($M^{-1}cm^{-1}$)	$W' \times 10^{-14}$ (photons/cm^2/s)	(K·Z)	$\frac{\varepsilon \cdot W'}{K\,Z}$
300	918	.0303	51.6	$.539 \times 10^{14}$
310	356	.388	46.2	2.99×10^{14}
320	101	1.13	41.4	2.76×10^{14}
330	11	1.81	37.4	$.532 \times 10^{14}$
				$\sum_i = 6.82 \times 10^{14}$

Given that the quantum yield is .006, the mean photolysis rate constant can be computed using Equation (II-82) and the above information:

$$k_d = 2.3 \cdot 1.43 \times 10^{-16} \cdot \frac{450}{540} \cdot .0060 \cdot 1.6 \cdot 6.82 \times 10^{14}$$
$$= 1.8 \times 10^{-3}\ \text{day}^{-1}$$

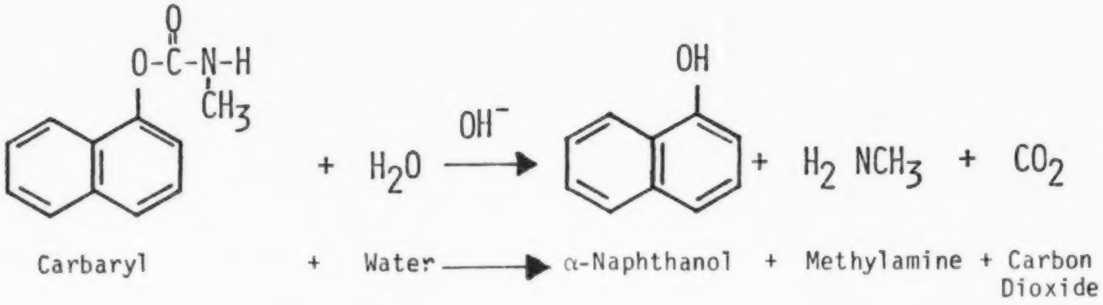
The small difference between the rate constants calculated in parts A and B is due to the difference in the reference solar intensities. The assumption made here that the spectral distribution of solar energy is independent of intensity is only approximately true. Consequently, the greater the discrepancy between the reference and local solar intensities, the greater the error in rate constants that can be expected. When the local exceeds the reference intensity, the actual rate constant is probably higher than the calculated value. When the reference exceeds the local intensity, the actual rate constant is probably lower than calculated.

END OF EXAMPLE II-7

2.5.3 Hydrolysis

Some toxic compounds can be altered by direct reaction with water. The chemical reaction of a compound with water is called hydrolysis. Typically in hydrolysis reactions hydroxide replaces another chemical group.

An example hydrolysis reaction for a toxic organic compound is given below:


O-C-N-H
CH3
+ H2O
OH⁻
OH
+ H2 NCH3 + CO2
Carbaryl + Water → α-Naphthanol + Methylamine + Carbon Dioxide

Generalized hydrolytic reactions of organic compounds are presented in Table II-30.

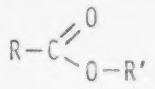
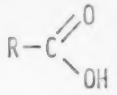
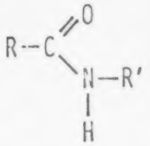
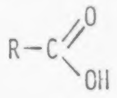
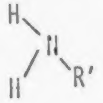
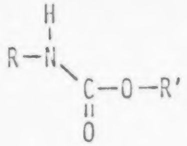
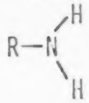
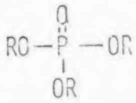
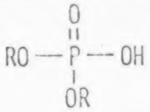
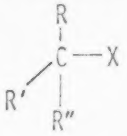
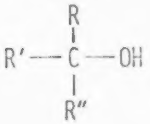
Hydrolysis reactions alter the reacting molecules but do not always produce less noxious products. For example the more toxic 2,4-D acid is produced from the hydrolysis of certain 2,4-D esters. Alternatively the hydrolysis of carbaryl (shown above) produces less toxic products, i.e. α-naphthanol and methylamine.

Hydrolysis products may be more or less volatile than the original compound. Hydrolysis products which ionize may have essentially zero volatility depending upon pH. Hydrolysis products are generally more readily biodegraded than the parent compounds, although there are some exceptions.

Hydrolysis reactions are commonly catalyzed by hydrogen or hydroxide ions. This produces the strong pH dependence often observed for hydrolysis reactions. Examples of this dependency are shown in Figure II-16, where the logarithms of reaction rate constants (k_H) are plotted versus pH. The

TABLE II-30

GENERALIZED HYDROLYTIC REACTIONS OF ORGANIC COMPOUNDS

Reactant	Reaction Conditions	Products
Carboxylic Acid Esters 	Acidic, Neutral, Basic	Carboxylic Acid + Alcohol  + R'OH
Amides 	Acidic, Basic	Carboxylic Acid + Amine  + 
Carbamates 	Acidic, Basic	Amine + Alcohol + Carbon Dioxide  R'OH CO_2
Organophosphates (and derivates)  $RO-\overset{O}{\overset{\|\|}{\underset{OR}{\underset{\|}{P}}}}-OR$	Basic (Acidic, Neutral)	Phosphate Diester + Alcohol  $RO-\overset{O}{\overset{\|\|}{\underset{OR}{\underset{\|}{P}}}}-OH$ ROH
Halogenated Alkanes 	Neutral, Basic	Alcohol + Halide Ion  $R'-\overset{R}{\overset{\|}{\underset{R''}{\underset{\|}{C}}}}-OH$ X^-

Source: I.J. Tinsley, Chemical Concepts in Pollutant Behavior, J. Wiley, New York (1979).

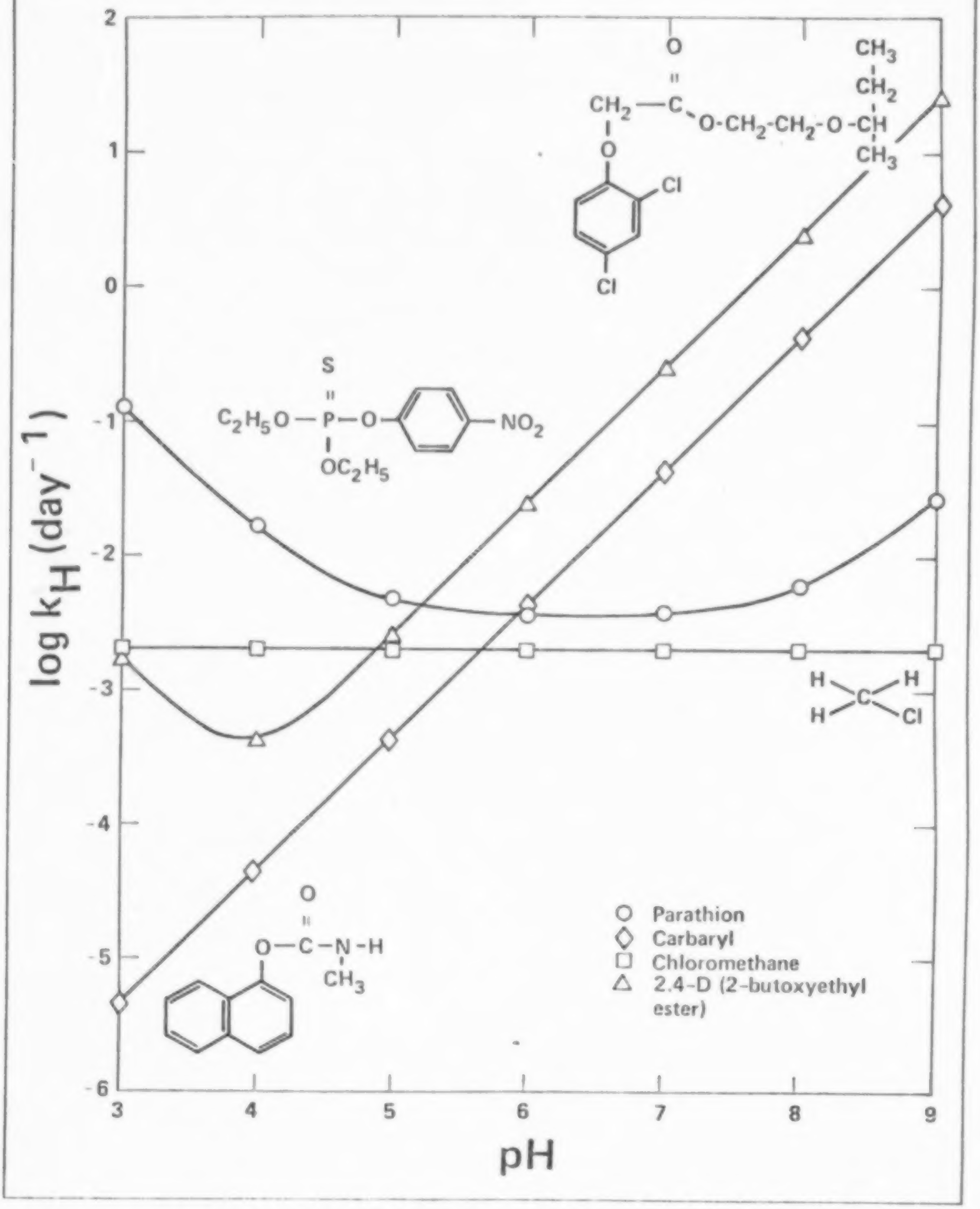


FIGURE II-16 pH DEPENDENCE OF HYDROLYSIS RATE CONSTANTS hydrolysis rate of carbaryl can be seen to increase logarithmically with pH. The rate at pH = 8 is ten times that at pH = 7 and 100 times that at pH = 6. The hydrolysis rate of parathion is high at low pH values, reaches a minimum at pH = 6, and then increases with increasing pH. The hydrolysis rate of chloromethane shows minimal dependence on pH over the range presented.

Adsorption can also influence hydrolysis rates. Adsorption of an organic molecule protects it from acid or base catalyzed hydrolysis (Wolfe, 1981). The amount of adsorption can be predicted using the principles presented in Section 2.3.2.

Microbially mediated hydrolysis reactions are responsible for the breakdown of many complex molecules, including natural polymers such as cellulose. Microorganisms catalyze hydrolysis reactions in the process of using organic compounds as energy and/or carbon sources. In cometabolism microbes may hydrolyze toxic organic compounds to hasten their removal from cell protoplasm. Microbially mediated processes are covered under the general heading of biodegradation in Section 2.5.1. Here only abiotic hydrolysis is treated.

Abiotic hydrolysis reactions are represented by rate expressions which are first order in the concentration of the compound being hydrolyzed:

$$R = \frac{\partial C}{\partial t} = -k_H C_T \qquad \text{(II-84)}$$

where R = the rate of hydrolysis, mole liter^{-1} sec^{-1} or µg liter^{-1} sec^{-1}

k_H = specific hydrolysis rate constant, sec^{-1}

C_T = the dissolved plus sorbed phased concentration of compound C, mole liter^{-1} or µg liter^{-1}

In the literature k_H is typically defined as:

$$k_H = k_n + k_a [H^+] + k_b [OH^-] \qquad \text{(II-85)}$$

In this document the specific hydrolysis rate constant, k_H, is defined to include the effects of adsorption:

$$k_H = \left[k_n + \alpha_w \left(k_a [H^+] + k_b [OH^-]\right)\right] \qquad \text{(II-86)}$$

where k_n = the neutral hydrolysis rate constant, sec^{-1}

α_w = the decimal fraction of the total amount of compound C which is dissolved (Calculation procedures in Section 2.3.2)

k_a = the acid catalyzed hydrolysis rate constant, liter $mole^{-1}$ sec^{-1}

$[H^+]$ = the molar concentration of hydrogen ion, mole $liter^{-1}$ $([H^+] \cong 10^{-pH})$

k_b = the base catalyzed hydrolysis rate constant, liter $mole^{-1}$ sec^{-1}

$[OH^-]$ = the concentration of hydroxide ion, mole $liter^{-1}$ $[OH^-] = 10^{(pH-pK_w)} \cong 10^{(pH-14)}$

Equation II-86 is a convenient definition of k_H because specific rates constants which act on the dissolved and total concentrations do not have to be used separately.

Values for the three rate constants k_n, k_a, k_b for selected compounds are presented in Table II-31. Additional values can be found in the literature (e.g. Mabey and Mill, 1978). The three constants can also be determined by simple laboratory tests.

Water body pH values must be obtained for hydrolysis reactions which are pH dependent (i.e. those for which $k_a \neq 0$ and/or $k_b \neq 0$). It should be noted that in poorly buffered waters (alkalinity $\leq$50 mg/l as $CaCO_3$), pH values may change by 1-2 units daily due to natural processes alone. In

TABLE II-31

HYDROLYSIS RATE PARAMETERS AND ESTIMATED ENVIRONMENTAL HYDROLYSIS RATES

Compound	Hydrolysis Rate Parameters $k_a(M^{-1}day^{-1})$	$k_n(day^{-1})$	$k_b(M^{-1}day^{-1})$	Environmental Hydrolysis Rates (pH=7) $k_H(day^{-1})$	$t_{½}$(days)	Ref. Temp. (°C)	Ref.
Pesticides							
Endosulfon	-	-	3.3×10^5	3.5×10^{-2}	21	27	a
Heptachlor	?	?	?	.7	1.	30	a
Carbaryl	-	-	4.3×10^5	4.3×10^{-2}	16.	27	b
Propham	-	-	.66	6.6×10^{-8}	1.1×10^7	27	b
Chlorpropham	-	-	1.7	1.7×10^{-7}	4.0×10^6	27	b
2,4-D(2-Butoxyethyl ester)	1.7	-	2.6×10^6	.26	2.7	28	c
2,4-D(Methyl ester)	-	-	1.5×10^6	.15	4.6	28	c
Parathion	1.3×10^2	3.6×10^{-3}	2.46×10^3	3.9×10^{-3}	1.8×10^2	?	d
Phosmet	?	?	?	2.3	.30	20	e
Dialifor	?	?	?	1.2	.58	20	e
Malathion	?	?	?	6.6×10^{-2}	11.	20	e
Captan	-	1.6	4.9×10^7	5.6	.13	27	f
Atrazine	3.4	6.6	-	6.6	.10	25	f
Methoxychlor	-	2.6×10^{-3}	31.	2.6×10^{-3}	2.7×10^2	25	f
Halogenated Hydrocarbons							
Chloromethane	-	2.1×10^{-3}	.53	2.1×10^{-3}	3.4×10^2	25	f
Bromomethane	-	3.5×10^{-2}	12.	3.5×10^{-2}	20.	25	f
Chloroethane	-	1.8×10^{-2}	-	1.8×10^{-2}	38.	25	f
Dichloromethane	-	2.8×10^{-6}	1.8×10^{-3}	2.8×10^{-6}	2.6×10^5	25	f
Trichloromethane	-	-	6.0	6.0×10^{-7}	1.3×10^6	25	f
Bromodichloromethane	-	-	1.4×10^3	1.4×10^{-5}	5.0×10^4	25	f
Dibromochloromethane	-	-	69.	6.9×10^{-6}	1.0×10^5	25	f
Tribromomethane	-	-	28.	2.8×10^{-6}	2.5×10^5	25	f
Hexachlorocyclopentadiene	-	4.8×10^{-2}	-	4.8×10^{-2}	14.	25	a
Halogenated Ethers							
Bis(chloromethyl) ether	-	1.6×10^3	-	1.6×10^3	4.5×10^{-4}	20	a
2-Chloroethyl vinyl ether	3.8×10^2	-	-	3.8×10^{-5}	1.8×10^4	25	a
Phthalate Esters							
Dimethyl ester	1.	-	6.0×10^3	6.0×10^{-4}	1.2×10^3	30	g
Diethyl ester	1.	-	1.9×10^3	1.9×10^{-4}	3.7×10^3	30	g
Di-_n_-butyl ester	1.	-	9.1×10^2	9.1×10^{-5}	7.6×10^3	30	g
Di-_n_-octyl ester	1.	-	1.4×10^3	1.4×10^{-4}	4.9×10^3	30	g
Di(2-ethylhexyl) ester	1.	-	9.6	9.6×10^{-7}	7.2×10^5	30	g
Monocyclic Aromatics							
Pentachlorophenol	1.1×10^4	5.8×10^{-3}	3.3	6.9×10^{-3}	1.0×10^2	?	d

Notes

"?" denotes rate parameter not given and not estimable from data in reference
"-" denotes zero or very small rate parameter

References:

[a] Callahan et al. (1979)
[b] Wolfe et al. (1978)
[c] Zepp et al. (1975)
[d] Park et al. (1980)
[e] Tinsley (1979)
[f] Mabey and Mill (1978)
[g] Wolfe et al. (1980)

these cases either additional data must be gathered to characterize the system's pH regime or conservatively low values of k_H must be used.

EXAMPLE II-8

A biodegradation rate constant, k_B for the fungicide Captan has been given as 0.5 per day. Compare this with the abiotic hydrolysis rate constant, k_H, at pH = 8.4, a temperature of 25°C, and with 90 percent of the compound adsorbed on suspended matter. Values for k_a, k_b, and k_n can be found in Table II-31.

$k_a = 0$
$k_b = 4.9 \times 10^7 \text{ day}^{-1}$
$k_n = 1.6 \text{ day}^{-1}$

$$k_H = \left[\alpha_w \left(k_a[H^+] + k_b[OH^-]\right)\right] + k_n$$

$$[OH^-] \cong 10^{pH-14} = 10^{8.4-14} = 10^{-5.6} = 2.51 \times 10^{-6}$$

thus

$$k_H = \left[(1.0-0.9)\cdot(4.9 \times 10^7 \times 2.5 \times 10^{-6})\right] + 1.6$$

$$= 12.3 + 1.6 = 13.9 \text{ day}^{-1}$$

Comparing k_H to k_B,

$$\frac{k_H}{k_B} = \frac{13.9}{0.5} = 27.8$$

Comparison of k_H with k_B for the above situation shows that the abiotic hydrolysis rate is about 28 times faster than the biodegradation rate. Biodegradation could be neglected here with minimal effect on the results.

END OF EXAMPLE II-8

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Zepp, R.G. and P.F. Schlotzhauer. 1981. Comparison of Photochemical Behavior of Various Humic Substances in Water: III. Spectroscopic Properties of Humic Substances, Chemosphere. Volume 10, No. 5, pp. 479-486.

Zepp, R.G., N.L. Wolfe, J.A. Gordon, and G.L. Baughman. 1975. Dynamics of 2,4-D Esters in Surface Waters. Environmental Science and Technology, Volume 9, No. 13, pp. 1144-1150.

CHAPTER 3
WASTE LOADING CALCULATIONS

3.1 INTRODUCTION

This chapter outlines basic procedures that can be used to generate estimates of diffuse (nonpoint) and point source loads. Loading functions for the following pollutants will be considered for nonpoint sources:

- Sediment
- Nutrients (phosphorus and nitrogen)
- Organic matter
- Salinity in irrigation return flow
- Toxic organic pollutants
- Metals

Both cultivated and noncultivated agricultural land as well as urban areas are addressed in this report. For agricultural lands, long term sediment loads are calculated with the Universal Soil Loss Equation (USLE). This method has been adopted for a number of reasons, principal among them being the large data base that exists for the terms in the USLE. The modified USLE is presented as a method for estimating single event conventional pollutant loads. The loading of both nutrients and organic matter can be quantitatively related to sediment loading. Thus, the discussion of nutrients and organic matter logically follows the sediment loading calculations. These selected water quality parameters were chosen for inclusion in this report because they represent commonly occurring problems of major concern to planners.

Salinity in irrigation return flow is important in many areas in the arid western states. Considerable data are included in this report especially for the Colorado River basin and the irrigated regions in California (Section 3.2.8). Procedures are included for determining electrical conductivity and sodium adsorption ratio (SAR).

For urban areas two procedures are presented; the URS Urban Water Quality Management procedure and the SWMM Level One Screening procedure. In the former, solids loading rates are first calculated and then the loading rates of other pollutants are related to them. Pollutants considered in this section include BOD, phosphorus, nitrogen, coliforms, and heavy metals. In the SWMM procedure separate and combined sewers are considered as well as street sweeping efficiency. Single event procedures are also provided for urban areas.

Next, typical point source pollutant loads for municipal and industrial discharges are discussed. Whenever possible, however, local data should always be used, if available, in lieu of the "typical" loadings given here.

Within each major section a subsection on toxic organic pollutants is included. These sections cover the various ways in which toxicants accumulate on watershed surfaces and provide procedures to estimate washoff of toxicants in the sediment and water phases.

Each of the major divisions on nonpoint source calculations (agricultural and urban areas) in this chapter is essentially independent of every other. Accordingly, they can be used in any order. Within each section, the calculations performed can be used in two different ways. First, the magnitude of loadings can be compared for various alternatives (e.g., different land use schemes) to ascertain the significance of the changes. Second, the loadings can be used in calculations presented in Chapter 4 to assess the water quality impacts of nonpoint source pollutants on rivers and streams. These data can then be used to determine input of nonpoint source pollutants to impoundments (Chapter 5) and estuaries (Chapter 6), as appropriate.

In writing this chapter the following sources have been heavily and freely drawn upon: "Loading Functions for Assessment of Water Pollution from Nonpoint Source (McElroy et al., 1976), "Water Quality Management Planning for Urban Runoff" (Amy, et al., 1974), "Storm Water Management Model Level I, Preliminary Screening Procedures" (Heaney, et al., 1976), "Predicting Rainfall Erosion Losses: A Guide to Conservation Planning" (Wischmeier and Smith, 1978) and "A Mathematical Model for Estimating

Pesticide Losses in Runoff" (Haith, 1980). Users should refer to these references for further details concerning the methodologies.

3.2 NONURBAN NONPOINT SOURCE LOADS

3.2.1 Annual Sediment Loads

Sediment loading is defined in this report as the quantity of soil material that is eroded and transported into the watercourse. Sediment loading is dependent on (a) on-site erosion, and (b) delivery, or the ability of runoff to carry the eroded material into the receiving waters.

The sediment loading function is based on the mechanisms of gross erosion and sediment delivery. The Universal Soil Loss Equation (Wischmeier and Smith, 1965) has been chosen to predict on-site surface (including sheet and rill) erosion, for the following reasons:

1. This equation is applicable to a wide variety of land uses and climatic conditions.

2. Data have been collected nationwide for factors included in the equation.

The sediment loading function has the form:

$$Y(S)_E = \sum_{i=1}^{n} [A_i \cdot (R \cdot K \cdot L \cdot S \cdot C \cdot P)_i S_d] \qquad \text{(III-1)}$$

where

$Y(S)_E$ = sediment loading from surface erosion, (tons/year, tonnes/year)

n = number of subareas in the area

3 OF 7

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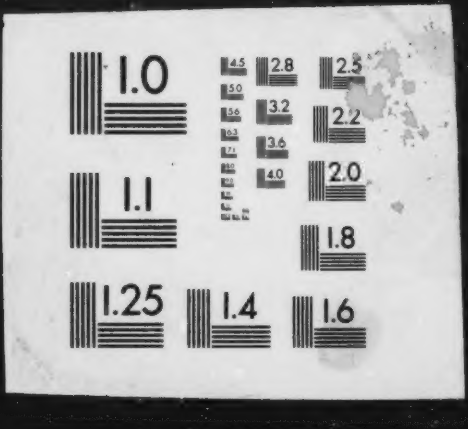

1.0
4.5
5.0
5.6
6.3
7.1
8.0
2.8
3.2
3.6
4.0
2.5
2.2
2.0
1.1
1.8
1.25
1.4
1.6

A_i = acreage of subarea i, (acres, ha)

R = the rainfall factor, expressing the erosion potential of average annual rainfall in the locality.

K = the soil-erodibility factor, commonly expressed in tons per acre per R unit

L = the slope-length factor, dimensionless ratio

S = the slope-steepness factor, dimensionless ratio

C = the cover factor, dimensionless ratio

P = the erosion control practice factor, dimensionless ratio and

S_d = the sediment delivery ratio, dimensionless.

Equation III-1 can be used to predict sediment loading resulting from sheet and rill erosion from cultivated and non-cultivated lands. Parameter values for silviculture, construction, and mining are less well documented than for agriculture, however. The user will thus find it relatively easy to use Equation III-1 for agriculture, and substantially more difficult for other sources. The equation does not predict sediment contributions from gully erosion, streambank erosion, or mass soil movement.

Estimation of surface erosion should be made for each relatively homogeneous land-use type. For a given land-use type, if 90 percent or more of the area is made up of one soil type, one may calculate soil loss for each soil type that makes up at least 10 percent of the land use, and then obtain a weighted average for the entire land-use area (U.S. Dept. of Agriculture, 1974). There is no limitation on how finely the watershed can be broken down into subwatersheds. This determination should be made based on information density, time and monetary restrictions, and level of accuracy desired in the results. Figure III-1 is a flow diagram showing the usage of Equation III-1 for predicting annual average sediment loads.

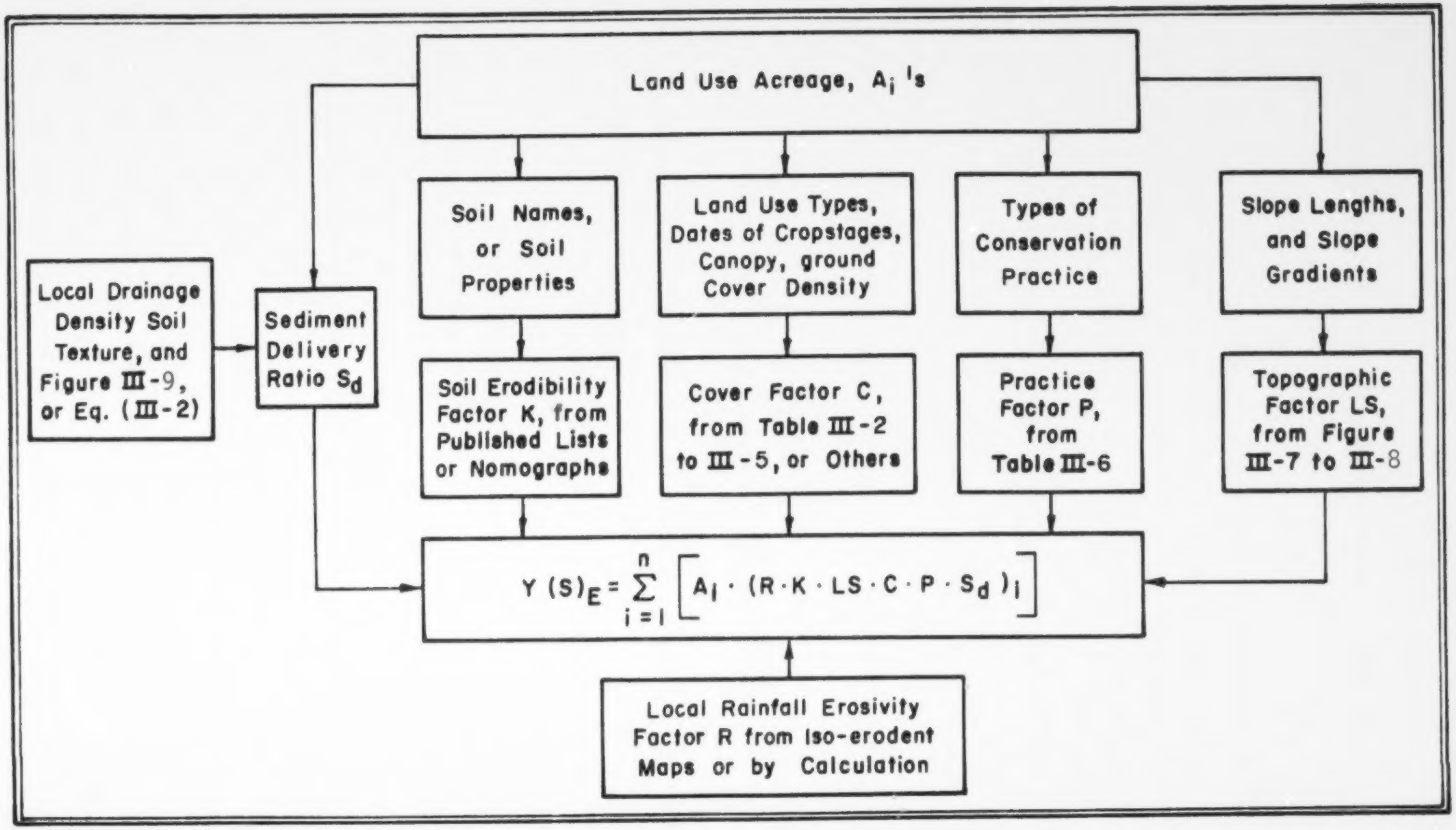

Land Use Acreage, A_i's
Local Drainage Density Soil Texture, and Figure III-9, or Eq. (III-2)
Sediment Delivery Ratio S_d
Soil Names, or Soil Properties
Soil Erodibility Factor K, from Published Lists or Nomographs
Land Use Types, Dates of Cropstages, Canopy, ground Cover Density
Cover Factor C, from Table III-2 to III-5, or Others
Types of Conservation Practice
Practice Factor P, from Table III-6
Slope Lengths, and Slope Gradients
Topographic Factor LS, from Figure III-7 to III-8
$Y(S)_E = \sum_{i=1}^{n} \left[A_i \cdot (R \cdot K \cdot LS \cdot C \cdot P \cdot S_d)_i \right]$
Local Rainfall Erosivity Factor R from Iso-erodent Maps or by Calculation

FIGURE III-1 FLOW DIAGRAM FOR CALCULATING SEDIMENT LOADING FROM SURFACE EROSION

3.2.1.1 Data Requirements

The following should be obtained:

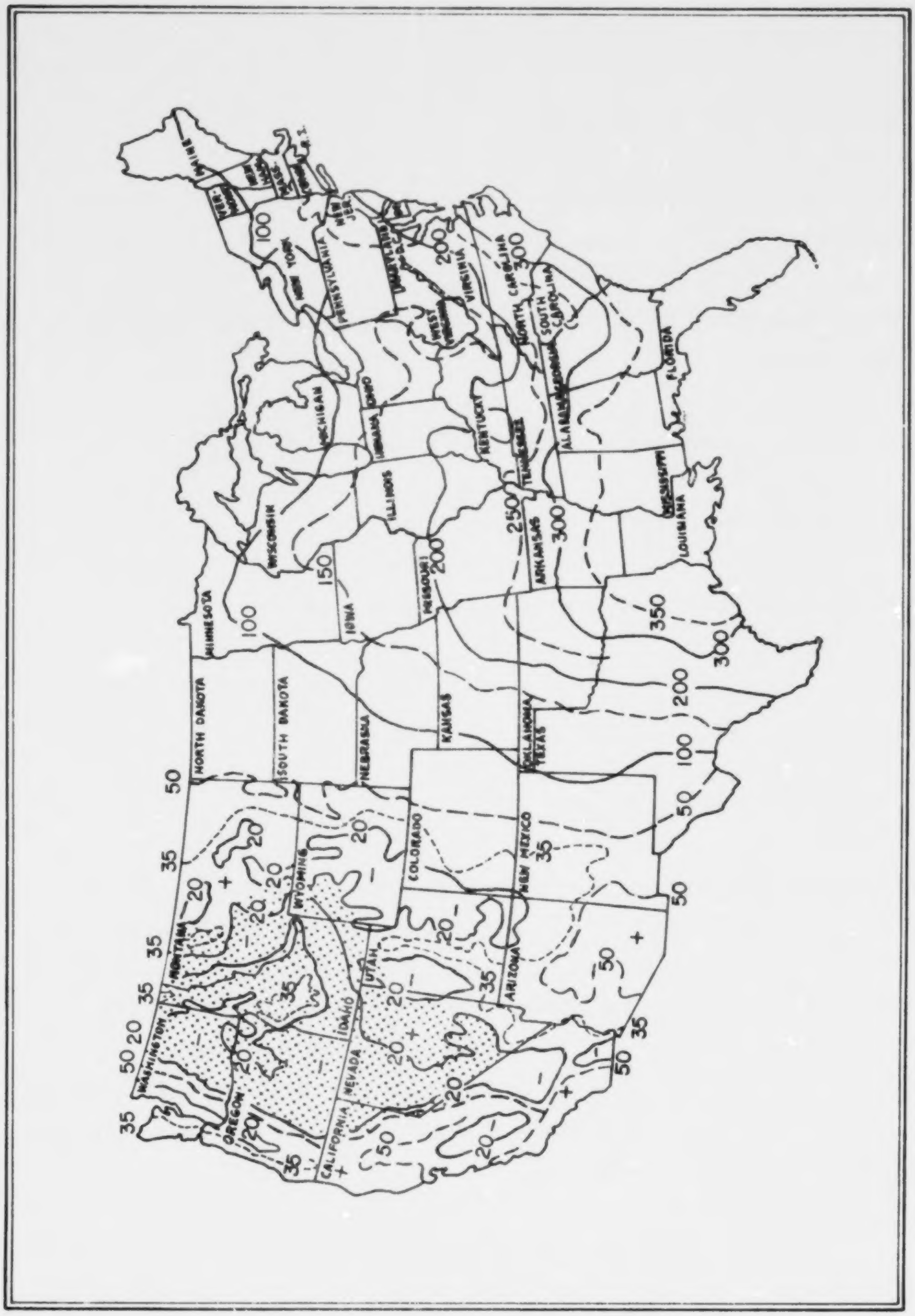
- total area, and land use acres in the area: cropland, pastureland, and woodland, etc.
- soil characteristic information (e.g. soil texture) for each land use.
- canopy and ground cover condition for each land use.
- good topographic maps
- the type and extent of conservation practices.

3.2.1.2 Determination of USLE Factors

3.2.1.2.1 The Rainfall Factor (R)

R is a factor expressing the erosion potential of precipitation in a locality. It is also called index of erosivity, erosion index, etc. It is the summation of the individual storm products of the kinetic energy of rainfall (denoted by E), and the maximum 30 minute rainfall intensity (denoted by I) for all significant storms within the period under consideration. The product EI reflects the combined potential of raindrop impact and runoff turbulence to transport dislodged soil particles from the site (Wischmeier and Smith, 1965).

Values of average annual rainfall-erosivity index, R, are shown in Figure III-2 for the continental U.S. and Figure III-3 for islands of Hawaii. On these maps, the lines joining points with the same erosion index value are called isoerodents. Points lying between the indicated isoerodents may be approximated by linear interpolation.


WASHINGTON
OREGON
CALIFORNIA
NEVADA
IDAHO
MONTANA
WYOMING
UTAH
ARIZONA
COLORADO
NEW MEXICO
NORTH DAKOTA
SOUTH DAKOTA
NEBRASKA
KANSAS
OKLAHOMA
TEXAS
MINNESOTA
IOWA
MISSOURI
ARKANSAS
LOUISIANA
WISCONSIN
ILLINOIS
MICHIGAN
INDIANA
OHIO
KENTUCKY
TENNESSEE
MISSISSIPPI
ALABAMA
GEORGIA
FLORIDA
SOUTH CAROLINA
NORTH CAROLINA
VIRGINIA
WEST VIRGINIA
PENNSYLVANIA
NEW YORK
NEW JER.
MARYLAND
MAINE
VER-MONT
NEW HAMP.
MASS.
CONN.
R.I.
35
50
20
35
35
35
20
20
20
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50
50
50
35
50
100
150
200
250
300
350
300
200
100
50
200
300
100
+
-

FIGURE III-2 AVERAGE ANNUAL VALUES OF THE RAINFALL-EROSIVITY FACTOR, R (EPA, 1975)

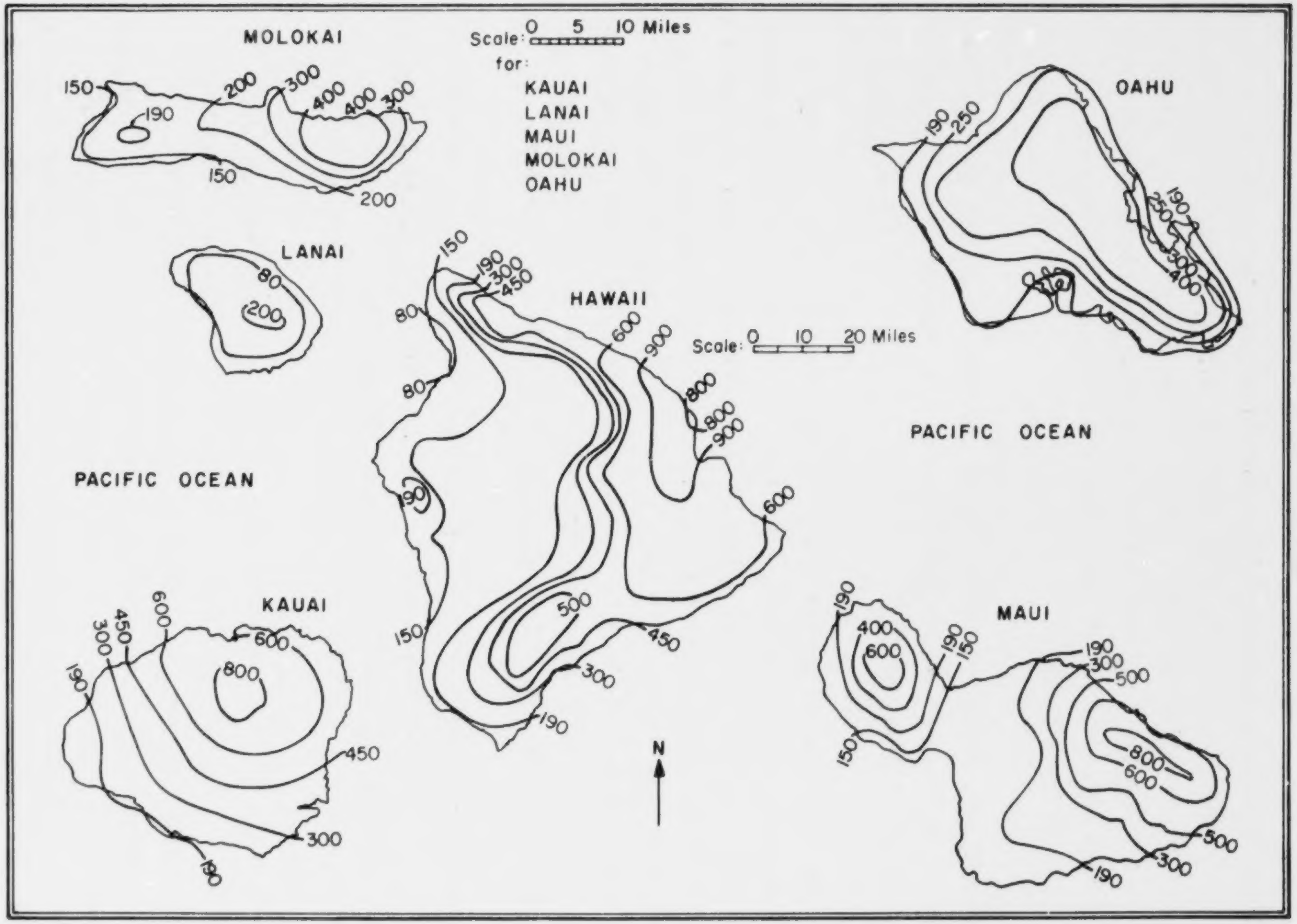
MOLOKAI
Scale: 0 5 10 Miles
for:
KAUAI
LANAI
MAUI
MOLOKAI
OAHU
150
190
200
300
400
400
300
150
200
LANAI
80
200
OAHU
190
250
190
250
300
400
HAWAII
150
190
300
450
80
80
600
900
800
800
900
190
600
500
450
300
190
150
Scale: 0 10 20 Miles
PACIFIC OCEAN
PACIFIC OCEAN
KAUAI
600
450
300
190
600
800
450
300
190
MAUI
190
400
600
190
150
150
190
300
500
800
600
500
300
190
N

Figure III-3 Mean Annual Values of Erosion Index for Hawaii (U.S.D.A., 1974)

Interpolation for values of R factors in the mountainous areas, particularly those west of the 104th meridian may not be appropriate because of the sporadic rainfall pattern. Values of the erosion index at specific areas can be computed from local recording rain gage records with the help of a rainfall-energy table and the computation procedure presented by Wischmeier and Smith (1978).

The USDA has recommended that 350 be the maximum used in the Gulf and southeastern states, shown in Figure III-2, until further research can validate values higher than 350.

In the northwestern United States, runoff from snowmelt contributes significantly to surface erosion. The annual index of R for some portions of this region is the combined effect of rainfall and snowmelt designated by R_r and R_s, respectively. The snowmelt factor (R_s) is important in Areas A-1, B-1, and C on Figure III-4 (also refer to Table III-1). The map values in the shaded region of the Northwest (see Figure III-2) represent values for the rainfall effect (R_r) only, and must be added with appropriate R_s values to account for the effect of runoff from thaw and snowmelt.

Interim procedures for calculating annual R values, which include both R_r and R_s, for the northwestern U.S. are described in Conservation Agronomy Technical Note No. 32, USDA/SCS, Portland, Oregon (1974), and are briefly presented below.

The annual R factor is obtained by using as a base the two year, six hour rainfall (2-6 rainfall). Relationships between R_r and 2-6 rainfall vary to conform to specific local climatic characteristics. These relationships are designated as Type I, Type IA, and Type II, and are shown in Figure III-5. Specific areas applicable to these curves are shown in Figure III-6. Type I curve is for the central valley and coastal mountains and valleys of southern California. Type IA curve applies to the coastal side of the Cascades in Oregon and Washington, the coastal side of the Sierra Nevada Mountains in northern California, and the coastal regions of Alaska. Type II curve applies to the remainder of the region. For 2-6 rainfall data, refer to Technical Paper No. 40, U.S. Department of Commerce,

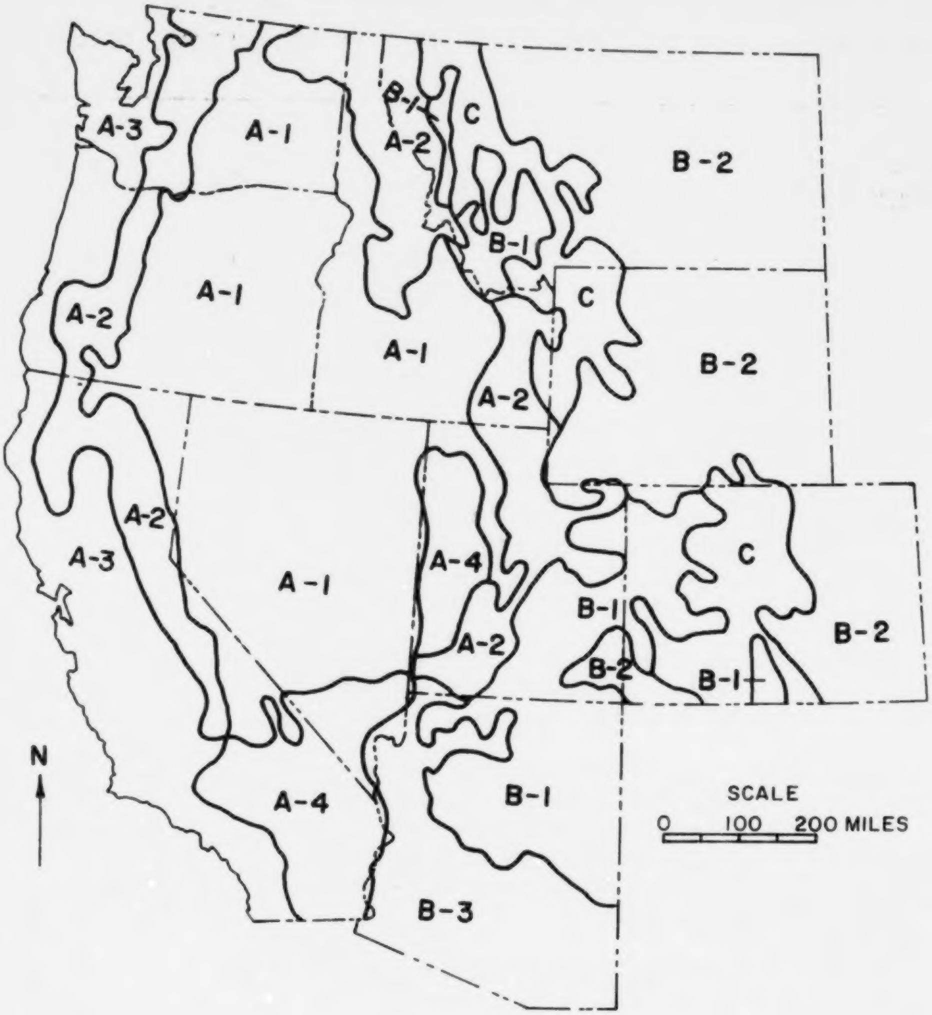
A-3
A-1
B-1
C
A-2
B-2
B-1
A-2
A-1
C
A-1
B-2
A-2
A-2
A-3
A-1
A-4
C
B-1
A-2
B-2
B-2
B-1
N
SCALE
0 100 200 MILES
A-4
B-1
B-3

FIGURE III-4 SOIL MOISTURE-SOIL TEMPERATURE REGIMES OF THE WESTERN UNITED STATES (U.S.D.A., 1974)

TABLE III-1

APPLICABILITY OF R_r AND R_s FACTORS IN THE AREAS WEST OF THE ROCKY MOUNTAINS (U.S. DEPT. OF AGRICULTURE, 1974a)

Areas (see Figure III-4)	Typical Locations	R_r	R_s
A-1	Washington, Idaho, Nevada, California, western Utah	X[a]	X
A-2	Cascades, Sierra, Tetons of Idaho, Wasatch Mountains	X	-[b]
A-3	West of Cascades, San Joaquin Valley, west of Sierras	X	-
A-4	Areas of southern California, east of Santa Anas, southern Nevada, intermountain Nevada, Salt Lake area, Utah	X	-
B-1	Western Montana, Colorado, eastern Utah, high elevations of Arizona	X	X
B-2	Great plains area of eastern Montana, Wyoming, Colorado (includes gently sloping mesas and upland at lower elevations of Monticello, Utah area)	X	-
C	Rainfall during summer is high; high elevations	X	X

[a] X needed

[b] - not needed

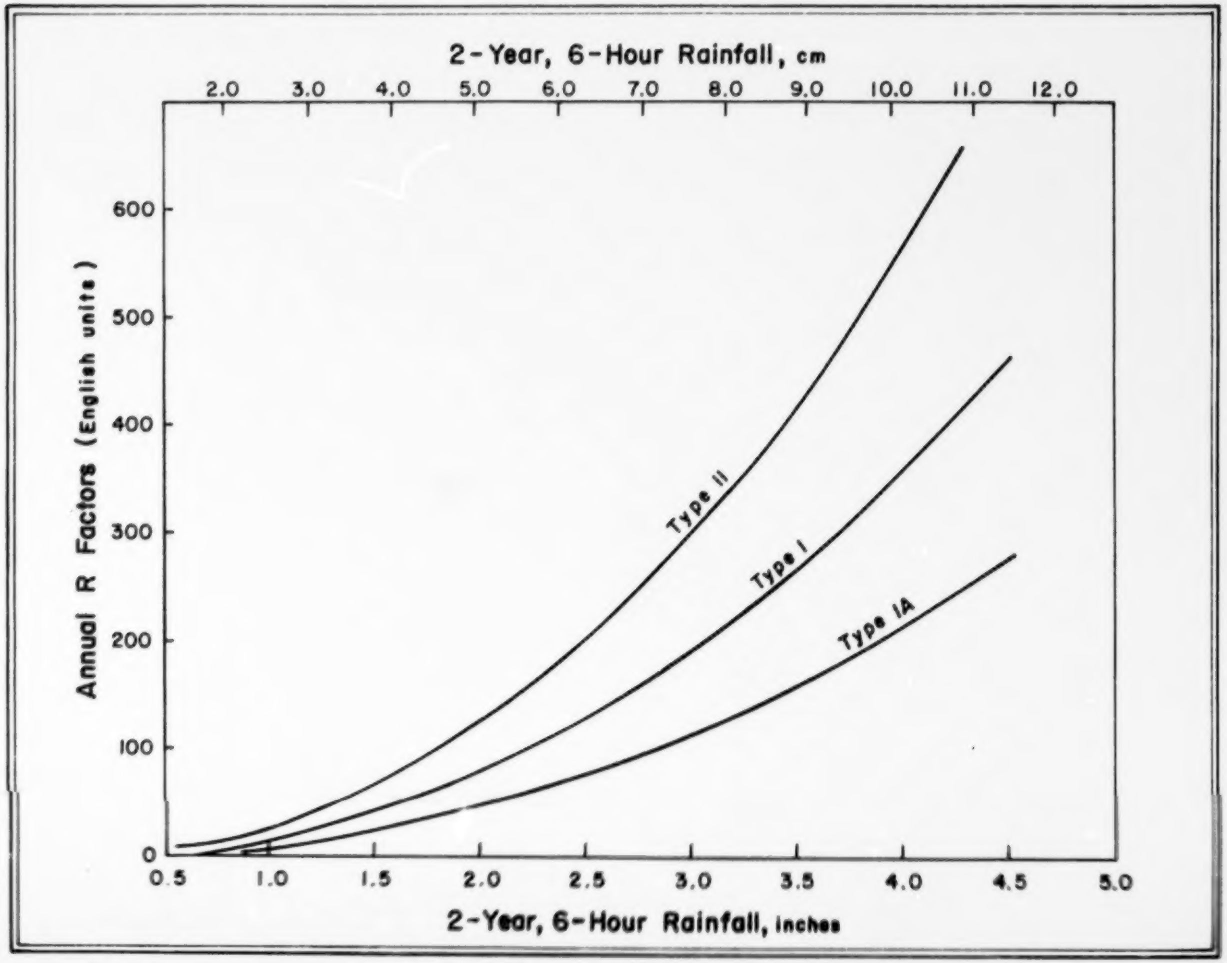

Figure III-5 Relationships between Annual Average Rainfall Erosivity Index and the 2-year, 6 hour Rainfall Depth for 3 Rainfall Types in Western U.S. (U.S.D.A., 1974)

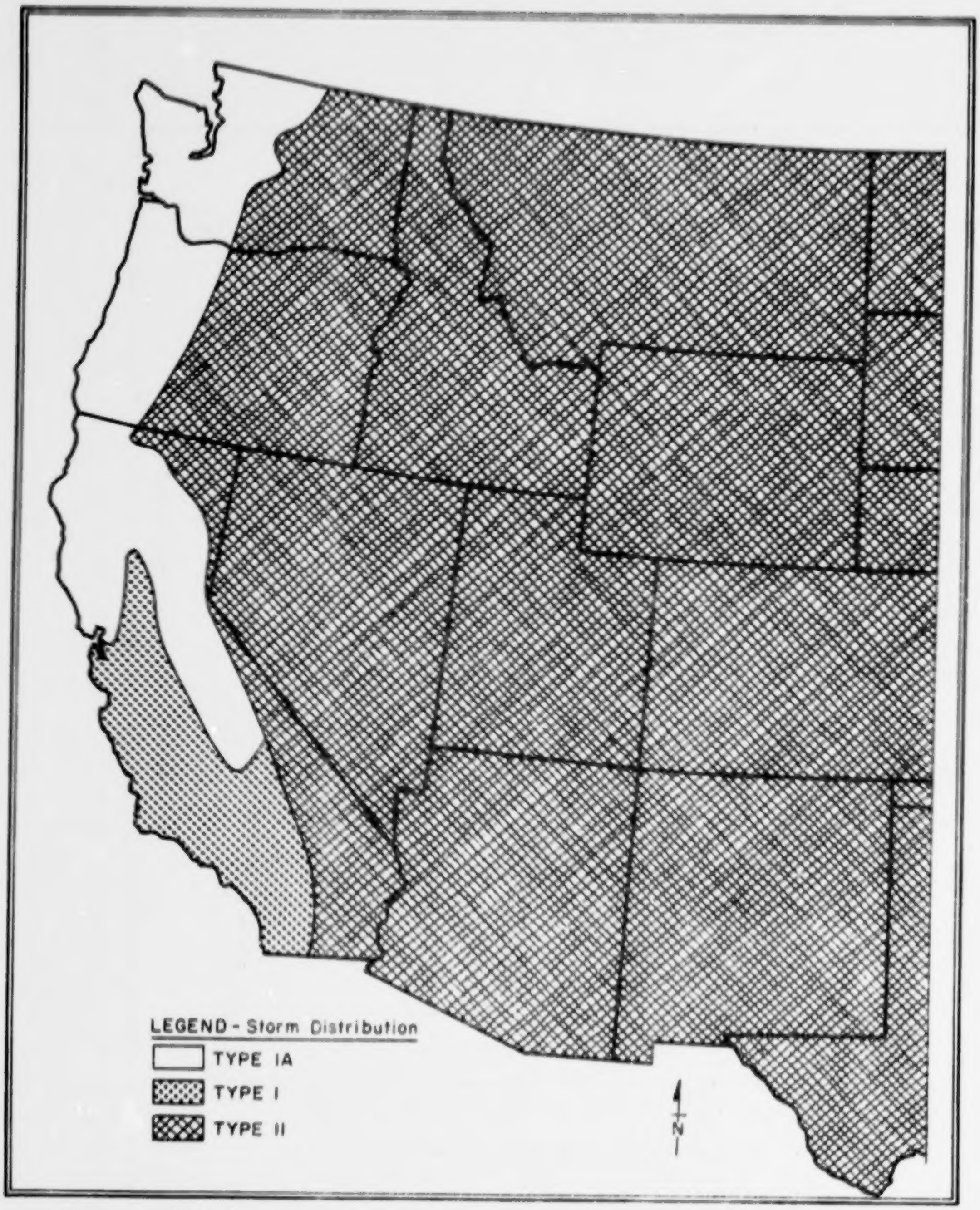
LEGEND - Storm Distribution
TYPE IA
TYPE I
TYPE II
N

Figure III-6 Storm Distribution Regions in Western U.S. (U.S.D.A., 1974)

Weather Bureau, Washington, D.C. (1961), or other suitable rainfall frequency analysis reports.

To obtain the annual R_s factor for a given location, obtain the average annual total precipitation by snowfall (in inches of water depth) and multiply it by the constant 1.5.

There are numerous sources of snowfall data for the United States. Some of the major sources are:

- The 1941 Yearbook of Agriculture, USDA, Washington, D.C.,
- "Climates of the States," Water Information Center, Inc., Port Washington, New York (1974), and
- Data resulting from the Western Federal-State-Private Cooperative Snow Surveys, coordinated by SCS/USDA, Portland, Oregon.

Data on snow density is necessary to convert depth of snow to depth of meltwater. Snow at the time of fall may have a density as low as 0.01 and as high as 0.15 g/ml. The average snow density for the United States is taken to be 0.10 (Garstka, 1964). If snowfall is recorded as inches of precipitation, no conversion is required.

The monthly distribution of the erosion index for the 37 states east of the Rocky Mountains has been reported in USDA-ARS Agriculture Handbook No. 282 (Wischmeier and Smith, 1965). Average monthly erosion index values are expressed as percentages of average annual values and plotted cumulatively against time in Appendix A.

The monthly distribution of erosion index for the islands of Hawaii also has been developed (U.S. Dept. of Agriculture, 1974b). These curves are shown in Appendix A. If monthly or seasonal sediment yields are required the annual R value can be factored using the percentages from these figures.

For the areas west of the Rockies in the continental United States, the monthly distribution of erosion index R is the summation of R_r and R_s. Where R_s values are not needed, the R and R_r curves are the same.

The R factor in equation III-1 can be expressed in metric units ((hundreds of metric tons/ha-cm) multiplied by (maximum 30-minute intensity, cm/hr)) by multiplying the English R values by 1.735.

3.2.1.2.2 The Soil-Erodibility Factor (K)

K factor is a quantitative measure of the rate at which a soil will erode, expressed as the soil loss (tons) per acre per unit of R, for a plot with 9 percent slope, 72.6 ft. long under continuous cultivated fallow. K factors for topsoils, as well as subsoils, for most soil series have been developed. Values of K for soils studied thus far vary from 0.12 to 0.70 tons/acre per unit R. Values can usually be obtained from the regional or state offices of the Soil Conservation Service.

K values of soils can also be predicted from soil properties. In Appendix B of this report, two methods are presented from which K values may be determined for topsoils and subsoils when the governing soil properties are known. The factor for conversion of K in English units to metric-tons per hectare per metric R unit is 1.292 (Wischmeier, 1972).

3.2.1.2.3 The Topographic Factor (LS)

Soil loss is affected by both length (L) and steepness of slope (S). These factors affect the capability of runoff to detach and transport soil material.

The slope length factor is the ratio of soil loss from a specific length of slope to that length (72.6 ft) specified for the K factor in the USLE. Slope length is defined as the distance from the point of origin of overland flow to either of the following: the point where the slope decreases to the extent that deposition begins or the point where runoff enters a well-defined channel. Slope length can be determined accurately by on-site inspection of a field, or by measurements from topographic maps. When the land is terraced, the terrace spacing should be used.

The slope gradient or percent slope factor is the ratio of soil loss from a specific percent slope to that slope (9 percent) specified for the K value in the USLE. A 9 percent slope has a factor value of 1. Slope data may be obtained from topographic maps, engineering or land level surveys, and other sources. A widely used method is to estimate slope from soil survey maps in which the soils have been mapped by slope range.

The slope length (L) and slope gradient (S) are usuallv combined in the USLE into a single dimensionless topographic factor, LS, which can be evaluated using a slope-effect chart.

The slope-effect chart in Figure III-7 is designed for the following areas shown in Figure III-4: A-1 in Washington, Oregon, and Idaho; and all of A-3 (U.S. Dept. of Agriculture, 1974a). For the remainder of the U.S., the slope-effect chart, Figure III-8, is to be used (U.S. Dept. of Agriculture, 1974a).

Slope-effect charts in Figure III-7 and III-8 can be used when uniform slopes are assumed. The following steps are to be used for obtaining LS values from these charts:

1. Enter the chart on the horizontal axis with the appropriate value of slope length.

2. Follow the vertical line for that slope length to where it intersects the curve for the appropriate percent slope.

3. Read across the point of intersection to the vertical axis. The number on the vertical axis is the LS value.

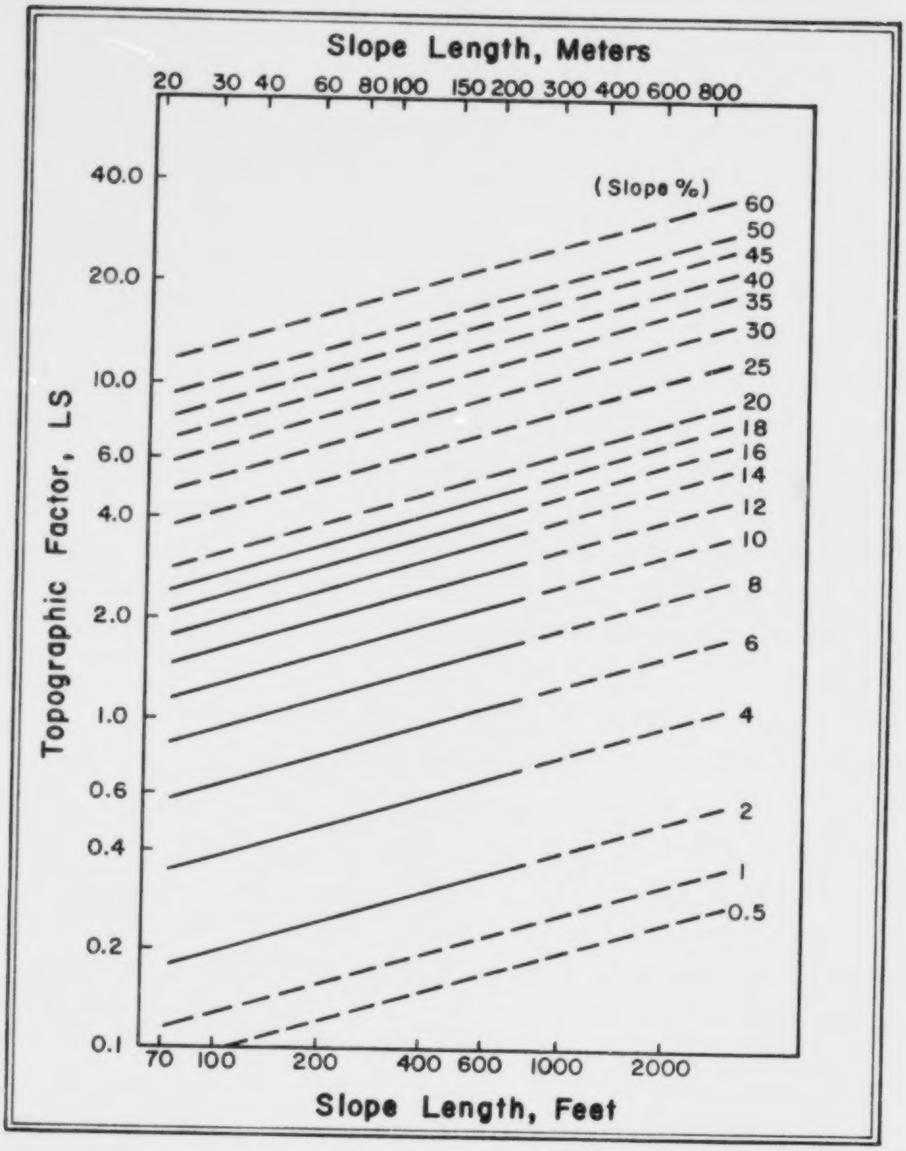

Figure III-7 Slope Effect Chart Applicable to Areas A-1 in Washington, Oregon, and Idaho and All of A-3 a,b/ (U.S. Dept. of Agriculture, 1974)

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a/ See Figure III-4.

b/ Dashed lines are extensions of LS formulae beyond values tested in studies.

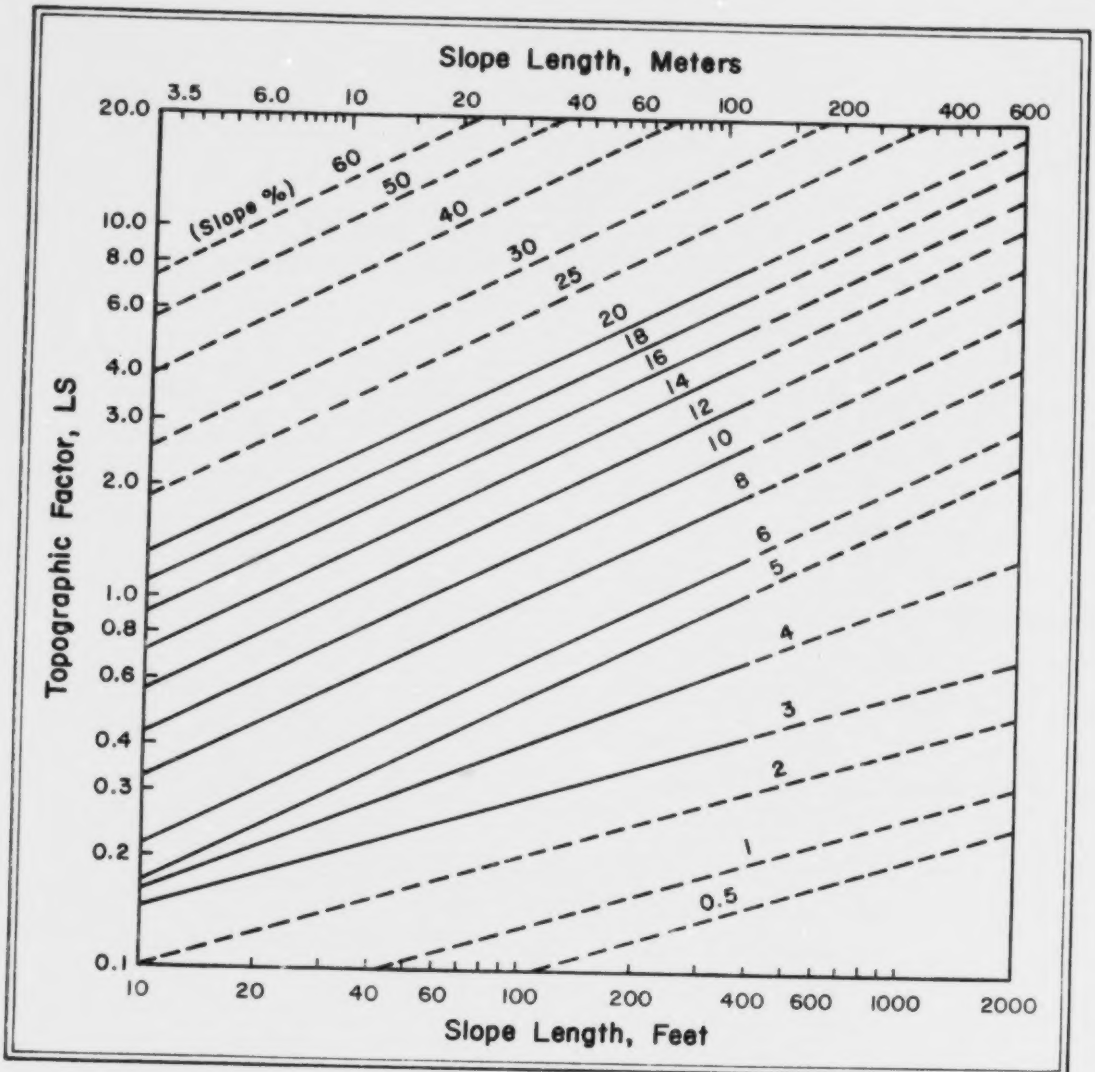

FIGURE III-8 SLOPE--EFFECT CHART FOR AREAS WHERE FIGURE III-7 IS NOT APPLICABLE a/ (U.S. DEPT. OF AGRICULTURE)

---

a/ THE DASHED LINES REPRESENT ESTIMATES FOR SLOPE DIMENSIONS BEYOND THE RANGE OF LENGTHS AND STEEPNESSES FOR WHICH DATA ARE AVAILABLE.

3.2.1.2.4 The Cover Management Factor (C)

In the USLE, the factor C represents the ratio of soil qualtity eroded from land that is cropped or treated under a specified condition to that which is eroded from clean-tilled fallow under identical slope and rainfall conditions. C ranges in value from near zero for excellent sod or a well-developed forest to 1.0 for continuous fallow, construction areas, or other extensively disturbed soil.

Values of factor C for croplands are highly variable with planting dates, type of vegetative cover, seeding method, soil tillage, disposition of residues, and general management level. Generalized C values for various types of crop management systems are listed in Table III-2. The reader is advised to consult with state conservation agronomists of SCS for appropriate C values for crops in the local area. The reader is also referred to USDA-ARS Agriculture Handbook No. 537 (Wischmeier and Smith, 1978) for a listing of approximated C values for various crops at each crop stage, as well as a working table for derivation of average C value for periods of crop rotation.

C values typical of permanent pasture, range, and idle lands, with varying cover and canopy conditions, are given in Table III-3. These values were developed by Wischmeier (1972). Wischmeier (1972) has also estimated C values for some woodland situations (Table III-4).

For urban and road areas, as well as construction sites, the factor C represents the effect of land cover or treatment that may be used to protect soil from being eroded. Table III-5 (Water Resources Administration, 1973) lists values of the C factors for various soil covers and treatments.

3.2.1.2.5 The Practice Factor (P)

The factor P accounts for control practices that reduce the erosion potential of runoff by their influence on drainage patterns, runoff concentration, and runoff velocity.

TABLE III-2

GENERALIZED VALUES OF THE COVER AND MANAGEMENT FACTOR, C, IN THE 37 STATES EAST OF THE ROCKY MOUNTAINS[1]

Line no.	Crop, rotation, and management[3]	Productivity level[2]	
		High	Mod.
		C value	
Base value: continuous fallow, tilled up and down slope		1.00	1.00
CORN			
1	C, RdR, fall TP, conv (1)	0.54	0.62
2	C, RdR, spring TP, conv (1)	.50	.59
3	C, RdL, fall TP, conv (1)	.42	.52
4	C, RdR, wc seeding, spring TP, conv (1)	.40	.49
5	C, RdL, standing, spring TP, conv (1)	.38	.48
6	C, fall shred stalks, spring TP, conv (1)	.35	.44
7	C(silage)-W(RdL, fall TP) (2)	.31	.35
8	C, RdL, fall chisel, spring disk, 40-30% rc (1)	.24	.30
9	C(silage), W wc seeding, no-till pl in c-k W (1)	.20	.24
10	C(RdL)-W(RdL, spring TP) (2)	.20	.28
11	C, fall shred stalks, chisel pl, 40-30% rc (1)	.19	.26
12	C-C-C-W-M, RdL, TP for C, disk for W (5)	.17	.23
13	C, RdL, strip till row zones, 55-40% rc (1)	.16	.24
14	C-C-C-W-M-M, RdL, TP for C, disk for W (6)	.14	.20
15	C-C-W-M, RdL, TP for C, disk for W (4)	.12	.17
16	C, fall shred, no-till pl, 70-50% rc (1)	.11	.18
17	C-C-W-M-M, RdL, TP for C, disk for W (5)	.087	.14
18	C-C-C-W-M, RdL, no-till pl 2d & 3rd C (5)	.076	.13
19	C-C-W-M, RdL, no-till pl 2d C (4)	.068	.11
20	C, no-till pl in c-k wheat, 90-70% rc (1)	.062	.14
21	C-C-C-W-M-M, no-till pl 2d & 3rd C (6)	.061	.11
22	C-W-M, RdL, TP for C, disk for W (3)	.055	.095
23	C-C-W-M-M, RdL, no-till pl 2d C (5)	.051	.094
24	C-W-M-M, RdL, TP for C, disk for W (4)	.039	.074
25	C-W-M-M-M, RdL, TP for C, disk for W (5)	.032	.061
26	C, no-till pl in c-k sod, 95-80% rc (1)	.017	.053
COTTON[4]			
27	Cot, conv (Western Plains) (1)	0.42	0.49
28	Cot, conv (South) (1)	.34	.40
MEADOW			
29	Grass & Legume mix	0.004	0.01
30	Alfalfa, lespedeza or Sericia	.020	
31	Sweet clover	.025	
SORGHUM, GRAIN (Western Plains)[4]			
32	RdL, spring TP, conv (1)	0.43	0.53
33	No-till pl in shredded 70-50% rc	.11	18

TABLE III-2 (Continued)

GENERALIZED VALUES OF THE COVER AND MANAGEMENT FACTOR, C, IN THE 37 STATES EAST OF THE ROCKY MOUNTAINS[1]- continued

Line no.	Crop, rotation, and management[3]	Productivity level[2]	
		High	Mod.
		C value	
SOYBEANS[4]			
34	B, RdL, spring TP, conv (1)	0.48	0.54
35	C-B, TP annually, conv (2)	.43	.51
36	B, no-till pl	.22	.28
37	C-B, no-till pl, fall shred C stalks (2)	.18	.22
WHEAT			
38	W-F, fall TP after W (2)	0.38	
39	W-F, stubble mulch, 500 lbs rc (2)	.32	
40	W-F, stubble mulch, 1000 lbs rc (2)	.21	
41	Spring W, RdL, Sept TP, conv (N & S Dak) (1)	.23	
42	Winter W, RdL, Aug TP, conv (Kans) (1)	.19	
43	Spring W, stubble mulch, 750 lbs rc (1)	.15	
44	Spring W, stubble mulch, 1250 lbs rc (1)	.12	
45	Winter W, stubble mulch, 750 lbs rc (1)	.11	
46	Winter W, stubble mulch, 1250 lbs rc (1)	.10	
47	W-M, conv (2)	.054	
48	W-M-M, conv (3)	.026	
49	W-M-M-M, conv (4)	.021	

[1] This table is for illustrative purposes only and is not a complete list of cropping systems or potential practices. Values of C differ with rainfall pattern and planting dates. These generalized values show approximately the relative erosion-reducing effectiveness of various crop systems, but locationally derived C values should be used for conservation planning at the field level. Tables of local values are available from the Soil Conservation Service.

[2] High level is exemplified by long-term yield averages greater than 75 bu. corn or 3 tons grass-and-legume hay; or cotton management that regularly provides good stands and growth.

[3] Numbers in parentheses indicate number of years in the rotation cycle. No. (1) designates a continuous one-crop system.

[4] Grain sorghum, soybeans, or cotton may be substituted for corn in lines 12, 14, 15, 17-19, 21-25 to estimate C values for sod-based rotations.

Abbreviations defined:

B - soybeans
C - corn
c-k - chemically killed
conv - conventional
cot - cotton
F - fallow
M - grass & legume hay
pl - plant
W - wheat
wc - winter cover

lbs rc - pounds of crop residue per acre remaining on surface after new crop seeding
% rc - percentage of soil surface covered by residue mulch after new crop seeding
70-50% rc - 70% cover for C values in first column; 50% for second column
RdR - residues (corn stover, straw, etc.) removed or burned
RdL - all residues left on field (on surface or incorporated)
TP - turn plowed (upper 5 or more inches of soil inverted, covering residues)

Source: U.S. EPA, 1975

TABLE III-3

"C" VALUES FOR PERMANENT PASTURE, RANGELAND, AND IDLE LAND (WISCHMEIER, 1972)[a]

Vegetal Canopy Type and Height of Raised Canopy[b]	Canopy Cover[c] (%)	Type[d]	Cover that Contacts the Surface Percent Ground Cover 0	 20	 40	 60	 80	 95-100
Column No.	2	3	4	5	6	7	8	9
No appreciable canopy		G	0.45	0.20	0.10	0.042	0.013	0.003
		W	0.45	0.24	0.15	0.090	0.043	0.011
Canopy of tall weeds or short brush (0.5 m fall height)	25	G	0.36	0.17	0.09	0.038	0.012	0.003
		W	0.36	0.20	0.13	0.082	0.041	0.011
	50	G	0.26	0.13	0.07	0.035	0.012	0.003
		W	0.26	0.16	0.11	0.075	0.039	0.011
	75	G	0.17	0.10	0.06	0.031	0.011	0.003
		W	0.17	0.12	0.09	0.067	0.038	0.011
Appreciable brush or brushes (2 m fall height)	25	G	0.40	0.18	0.09	0.040	0.013	0.003
		W	0.40	0.22	0.14	0.085	0.042	0.011
	50	G	0.34	0.16	0.085	0.038	0.012	0.003
		W	0.34	0.19	0.13	0.081	0.041	0.011
	75	G	0.28	0.14	0.08	0.036	0.012	0.003
		W	0.28	0.17	0.12	0.077	0.040	0.011

(continued)

TABLE III-3 (Continued)

Vegetal Canopy Type and Height of Raised Canopy b/	Canopy Cover c/ (%)	Type d/	Cover that Contacts the Surface					
			Percent Ground Cover					
			0	20	40	60	80	95-100
Column No.	2	3	4	5	6	7	8	9
Trees but no appreciable low brush (4 m fall height)	25	G	0.42	0.19	0.10	0.041	0.013	0.003
		W	0.42	0.23	0.14	0.087	0.042	0.011
	50	G	0.39	0.18	0.09	0.040	0.013	0.003
		W	0.39	0.21	0.14	0.085	0.042	0.011
	75	G	0.36	0.17	0.09	0.039	0.012	0.003
		W	0.36	0.20	0.13	0.083	0.041	0.011

a/ All values shown assume: (1) random distribution of mulch or vegetation, and (2) mulch of appreciable depth where it exists.

b/ Average fall height of waterdrops from canopy to soil surface: m = meters.

c/ Portion of total-area surface that would be hidden from view by canopy in a vertical projection (a bird's-eye view).

d/ G: Cover at surface is grass, grasslike plants, decaying compacted duff, or litter at least 5 cm (2 in.) deep.

W: Cover at surface is mostly broadleaf herbaceous plants (as weeds) with little lateral-root network near the surface and/or undecayed residue.

TABLE III-4

"C" VALUES FOR WOODLAND (WISCHMEIER, 1972)

Stand Condition	Tree Canopy Percent of Area[a]	Forest Litter Percent of Area[b]	Undergrowth[c]	"C" Factor
Well stocked	100-75	100-90	Managed[d]	0.001
			Unmanaged[d]	0.003-0.011
Medium stocked	70-40	85-75	Managed	0.002-0.004
			Unmanaged	0.01-0.04
Poorly stocked	35-20	70-40	Managed	0.003-0.009
			Unmanaged	0.02-0.09[e]

a/ When tree canopy is less than 20%, the area will be considered as grassland or cropland for estimating soil loss.

b/ Forest litter is assumed to be at least 2-in. deep over the percent ground surface area covered.

c/ Undergrowth is defined as shrubs, weeds, grasses, vines, etc., on the surface area not protected by forest litter. Usually found under canopy openings.

d/ Managed - grazing and fires are controlled.
Unmanaged - stands that are overgrazed or subjected to repeated burning.

e/ For unmanaged woodland with litter cover of less than 75%, C values should be derived by taking 0.7 of the appropriate values in Table III-3. The factor of 0.7 adjusts for the much higher soil organic matter on permanent woodland.

TABLE III-5

"C" VALUES FOR CONSTRUCTION SITES
(WATER RESOURCES ADMINISTRATION, 1973)

Type of Cover	C Value
None (fallow)	1.00
Temporary seedings	
First 60 days	0.40
After 60 days	0.05
Permanent seedings	
First 60 days	0.40
After 60 days	0.05
After 1 year	0.01
Sod (laid immediately)	0.01

	Rate of Application			Maximum Allowable Slope Length	
Mulch	In Metric Tons Per Hectare	In Tons Per Acre	C Value	(ft)	(m)
Hay or straw	1/2	1/2	0.34	20	6
	1	1	0.20	30	9
	1-1/2	1-1/2	0.10	40	12
	2	2	0.05	50	15
Stone or gravel	14	15	0.80	15	5
	55	60	0.20	80	24
	120	135	0.10	175	53
	220	240	0.05	200	61
Chemical mulches					
First 90 days		a/	0.50	50	15
After 90 days		a/	1.00	50	15
Woodchips	2	2	0.80	25	8
	4	4	0.30	50	15
	6	7	0.20	75	23
	11	12	0.10	100	30
	18	20	0.06	150	46
	23	25	0.05	200	61

a/ As recommended by manufacturer.

For croplands, control practices refer to contour tillage, cross-slope farming, and contour strip-cropping. The practice value P is the ratio of soil loss from a specified conservation practice to the soil loss occurring with up-and-downhill tillage, when other conditions remain constant. Table III-6 (USEPA, 1975) shows P values currently in common usage.

3.2.1.2.6 Sediment Delivery Ratio (S_d)

The sediment-delivery ratio, in this report, is defined as the fraction of the gross erosion which is delivered to some point in the stream system downstream of the source area. The classical method for determining an average delivery ratio is by comparing the magnitude of the sediment yield at a given point in a watershed (generally at a reservoir or a stream sediment measuring station), and the total amount of erosion. The quantities of gross erosion from sloping uplands are computed by erosion prediction equations for surface erosion, and estimated by various procedures for gullies, stream channels, and other sources. The sediment yield at a given downstream point is obtained through direct measurements. Estimates of the delivery ratio for some specific watersheds, particularly in the humid sections of the country, can be obtained from the Soil Conservation Service, USDA.

Many delivery-ratio studies have been aimed at finding measurable influencing factors that can be related to sediment-delivery ratio. A popular means of developing such information is by statistical analysis using the sediment-delivery ratio as the dependent variable and measurable watershed factors as the independent, or controlling variables. Many physical and hydrologic factors may influence sediment-delivery ratios. Empirical relationships for delivery ratios have been proposed and some are presented below. Estimates of sediment loading can be made through the use of these relationships, but such estimates should be tempered with judgment and consideration of other influencing factors not included in the quantitative expressions. The user is encouraged to consult with local experts and should use local data when available.

TABLE III-6

PRACTICE FACTORS (P) USED IN SEDIMENT LOADING EQUATION

Practice	Land slope (percent)				
	1.1-2	2.1-7	7.1-12	12.1-18	18.1-24
	(Factor P)				
Contouring (P_c)	0.60	0.50	0.60	0.80	0.90
Contour strip cropping (P_{sc})					
R-R-M-M[1]	0.30	0.25	0.30	0.40	0.45
R-W-M-M	0.30	0.25	0.30	0.40	0.45
R-R-W-M	0.45	0.38	0.45	0.60	0.68
R-W	0.52	0.44	0.52	0.70	0.90
R-O	0.60	0.50	0.60	0.80	0.90
Contour listing or ridge planting (P_{cl})	0.30	0.25	0.30	0.40	0.45
Contour terracing (P_t)[2]	[3] $0.6/\sqrt{n}$	$0.5/\sqrt{n}$	$0.6/\sqrt{n}$	$0.8/\sqrt{n}$	$0.9/\sqrt{n}$
No support practice	1.0	1.0	1.0	1.0	1.0

[1] R = rowcrop, W = fall-seeded grain, O = spring-seeded grain, M = meadow. The crops are grown in rotation and so arranged on the field that rowcrop strips are always separated by a meadow or winter-grain strip.

[2] These P_t values estimate the amount of soil eroded to the terrace channels and are used for conservation planning. For prediction of off-field sediment, the P_t values are multiplied by 0.2.

[3] n = number of approximately equal-length intervals into which the field slope is divided by the terraces. Tillage operations must be parallel to the terraces.

Source: U.S. EPA, 1975.

The MITRE Corporation (1974) reported that the sediment delivery ratio for construction sites can be approximated by a function of the overland distance between the construction site and the receiving water:

$$S_d = D^{-0.22} \qquad \text{(III-2)}$$

where

D = overland distance between the erosion site and the receiving water, (ft).

The above equation was empirically derived from available data. The data base for the derivations includes values of D from 0 to 800 ft. MITRE suggests that this function should be further tested, particularly in areas of the Midwest and Central U.S.

For mining sites, logging roads and fire lanes, sediment delivery ratio relationships have not yet been established due to lack of systematically measured data. It is suggested that the delivery ratio developed by MITRE and expressed in Equation III-2 be used as the first approximation for these sites. This should be verified when appropriate data become available.

Sediment delivery ratios have been evaluated in many areas of the country, particularly the eastern half of the United States. The delivery ratio usually depicts a general trend in basins that are relatively homogeneous with respect to soils, land cover, climate, and topography. The Soil Conservation Service (1973) analyzed data from stream and reservoir sediment surveys from widely scattered areas.

This analysis shows that sediment delivery ratios vary inversely with "drainage basin size". It also indicates the effect of soil texture of upland soil on the sediment delivery ratio.

The delivery ratio relationships reported by SCS (1973) were used by an MRI study group in developing delivery ratios for sediment loading to watercourses. The result is shown in Figure III-9. The horizontal scale of the figure is the reciprocal of drainage density which is defined as the

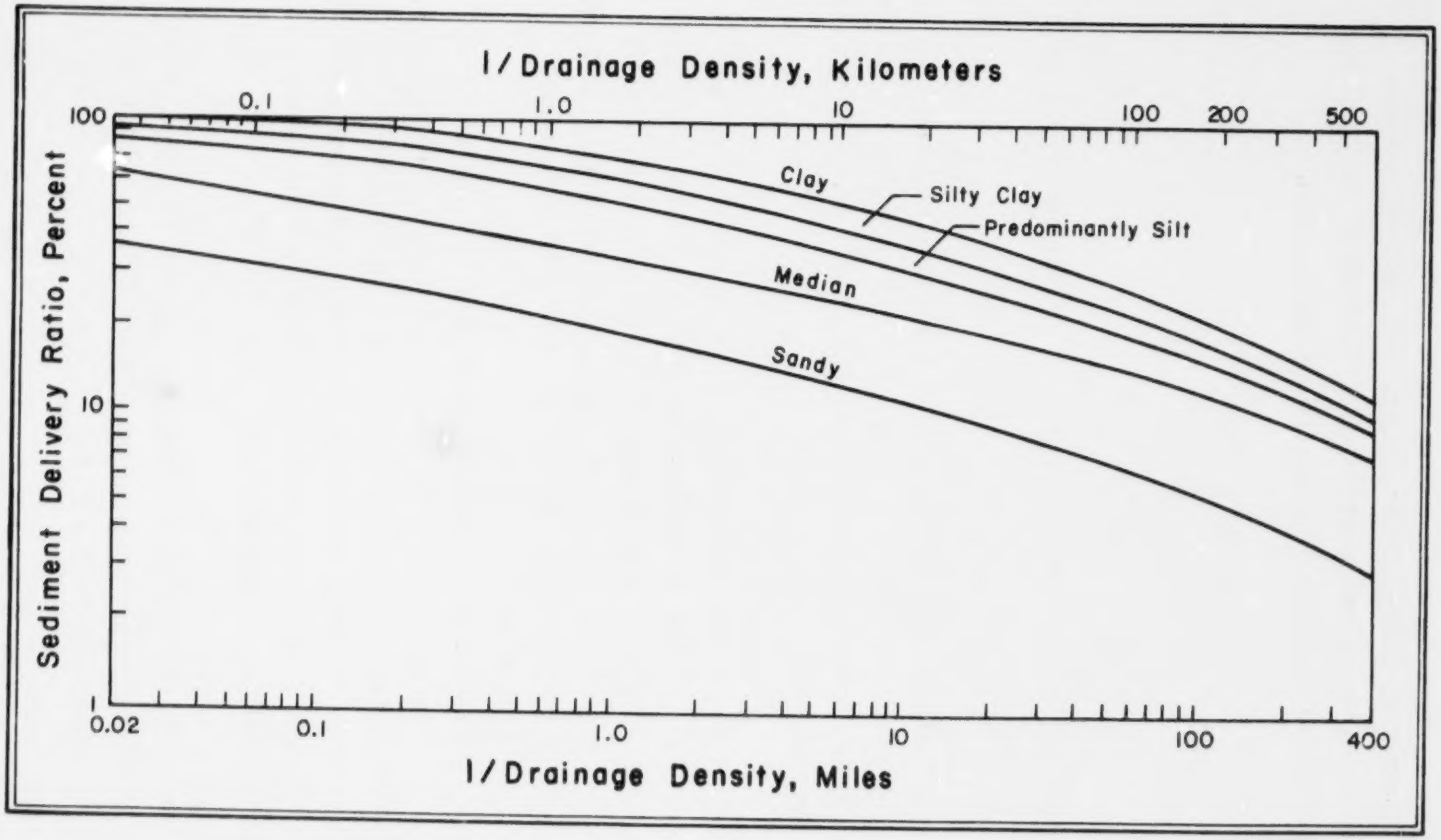

Figure III-9 Sediment Delivery Ratio for Relatively Homogeneous Basins (McElroy, *et al.*, 1976)

ratio of total channel-segment lengths (accumulated for all orders within a basin) to the basin area. The reciprocal of drainage density may be thought of as an expression of the closeness of spacing of channels, or the average distance for soil particles to travel from the erosion site to the receiving water. The drainage density is found by dividing the total length of perennial streams in the waters and by the area of the watershed.

The delivery ratio relationship shown in Figure III-9 also takes into account the effect of soil texture. For example, if soil texture of upland soil is essentially silt or clay, the sediment delivery ratio will be higher than when the soil texture is coarse.

The following steps are to be used to obtain the delivery ratio (S_d) from Figure III-9.

1. Enter the figure on the horizontal axis with the value of the reciprocal of drainage density (1/DD).

2. Move vertically from the value of 1/DD to where it intersects the curve for the appropriate soil texture.

3. Read across from the point of intersection to the vertical axis. That number represents the delivery ratio, S_d.

A great range of values of drainage density exists in the United States, from 2 km/km^2 (3 miles/mile^2) for the Appalachian Plateau Province (Smith, 1950) to 500 km/km^2 (800 miles/mile^2) in Badlands at Perth Amboy, New Jersey (Schumm, 1956). In general, according to Strahler (1964), low drainage density is found in regions of highly resistant or highly permeable subsoil materials, under dense vegetative cover, and where relief is low. High drainage density is favored in regions of weak or impermeable materials, sparse vegetation, and mountainous relief.

Some typical values of drainage density for various locales in the U.S. are given in Table III-7. Local drainage density figures may be obtained from agencies such as the U.S. Geological Survey and the Army Corps of Engineers.

TABLE III-7

TYPICAL VALUES OF DRAINAGE DENSITY

Location	Drainage density km/km^2	Drainage density mile/mile^2	Reference
Appalachian Plateau Province	1.9-2.5	3.0-4.0	Smith (1950)
Central and eastern United States	5-10	8.0-16.0	Strahler (1952)
Dry Areas of the Rocky Mountain Region	31-62	50-100	Melton (1957)
The Rocky Mountain Region (except the above)	5-10	8.0-16	Melton (1957)
Coastal ranges of Southern California	12-25	20-40	Smith (1950) Melton (1957) Maxwell (1960)
Badlands in South Dakota	125-250	200-400	Smith (1958)
Badlands in New Jersey	183-510	310-820	Schumn (1956)

Measurements of drainage density can be made from a topographic map with a planimeter and chartometer. Care must be taken to include all permanent stream channels to their upper ends by checking in the field or with aerial photographs to verify topographic maps. A rapid approximation method for determining drainage density is suggested by Carlston and Langbein (1960).

3.2.1.3 Limitations and Accuracy of Sediment Loading Equation

The USLE predicts soil losses from sheet and rill erosion. It does not predict sediment from gullies, streambank erosion, landslides, road ditches, irrigation, or from wind erosion. The USLE was developed primarily for croplands, and has been chiefly based upon experimental plot data from the areas east of the Rocky Mountains. The loading function therefore is best defined for these areas of use. For croplands in the western United States and sources outside agriculture such as silviculture, construction, and mining, the factors have not been systematically developed, which seriously affects the ease of using the USLE for such sources.

The USLE was developed primarily as a means of predicting annual erosion losses. Although several methods have been proposed for using it to calculate losses from individual events the MUSLE (Williams, 1975) presented later in this chapter is recommended.

The loading function (Equation III-1) and supporting data in tables and figures were designed to predict longterm average loadings for specific conditions. Sediment loading for a specific year may be substantially greater or smaller than the annual averages because of differences in number, size, and timing of erosive rainstorms, and in other weather parameters. Table II of USDA *Agriculture Handbook* 282 (1965) contains a listing of 50, 20, and 5 percent probability values of R factor at 181 key locations in the area east of the Rocky Mountains. These may be used for further characterization of soil-loss hazards.

Because of year to year variations in climate and management factors, the average soil loss predicted by the USLE may be different from that occurring in any given year. Onstad et al. (1979) evaluated the precision of the USLE factors. The results (Table III-8) show that C is the most variable parameter followed by K, R, L and S. When the coefficients of variation for each parameter where used in an error propagation exercise, it was found that the coefficient of variation of soil loss prediction was roughly 107 percent.

EXAMPLE III-1

Assessing Sediment Loading from Surface Erosion

The watershed of interest has an area of 830 acres. It is located in Parke County, Indiana. Compute sediment loading from the watershed from sheet and rill erosion in terms of average annual loading.

Basic Information

Land use types:

- Cropland
- Pasture
- Woodland

Delivery ratio: 60 percent

Land information: (Cropland - 180 acres)

- Continuous corn on contours
- Conventional tillage, average yield, 40 to 45 bu
- Cornstalks are removed after harvest, winter crop seeded
- Spring turn plowed
- Soil - Fayette silt loam
- Slope - 6 percent
- Slope length - 250 ft

TABLE III-8

EROSION EQUATION FACTOR PRECISION ERROR

Factor	Number of		Range of means	Coefficient of Variation
	Reps	Treatments		
				%
Rainfall factor (R)	22 yr	42 loc.	57-231	34
Soil erodibility (K)	4 to 20 loc.	14 soils	0.11-0.41	39
Cropping management factor (C)	4 to 20 single plots	5 rotations	0.01-1.40	92
Slope steepness (s)	3	29	1.0-46.3	4
Slope steepness factor (S)			0.02-16.1	5
Slope length (l)	3	6	50-148	38
Slope length factor (L)			1.5-1.6	19

Source: Onstad, et al., 1979

Pasture: (220 acres)

- No appreciable canopy
- Cover at surface - grass and grasslike plants
- Percent of surface or ground cover - 80 percent
- Soil - Fayette silt loam
- Slope - 6 percent
- Slope length - 200 ft

Woodland: (430 acres)

- Medium stocked
- Percent of area covered by tree canopy - 50 percent
- Percent of area covered by litter - 80 percent
- Undergrowth - managed
- Soil - Bates silt loam
- Slope - 12 percent
- Slope length - 150 ft

Solution:

Cropland:

R = 200 (Figure III-2)
K = 0.37 (USDA-SCS)
LS = 1.08 (Figure III-8)
C = 0.49 (Table III-2)
P = 0.50 (Table III-6)
S = 0.60

Calculate average annual loading per acre.

$$Y(S)_{annual} = 200 \times 0.37 \times 1.08 \times 0.49 \times 0.50 \times 0.6$$
$$= 11.7 \text{ tons/acre-year}$$

Pasture:

R = 200
K = 0.37
LS = 0.95
C = 0.013 (Table III-3)
P = 1.0

S = 0.60

$$Y(S)_{annual} = 200 \times 0.37 \times 0.95 \times 0.013 \times 1.0 \times 0.6$$
$$= 0.548 \text{ tons/acre-year} = 1{,}100 \text{ lb/acre-year}$$

Woodland:

R = 200
K = 0.32
LS = 2.75
C = 0.003 (Table III-4)
P = 1.0
S = 0.60

$$Y(S)_{annual} = 200 \times 0.32 \times 2.75 \times 0.003 \times 1.0 \times 0.60$$
$$= 0.3168 \text{ tons/acre-year}$$

Calculations of Gross Loading

Average annual:

Cropland - 180 acres x 11.7 tons/acre-year	=	2114 tons/year
Pasture - 220 acres x 0.55 tons/acre-year	=	121 tons/year
Woodland - 430 acres x 0.32 tons/acre-year	=	138 tons/year
Total $Y(S)_E$	=	2374 tons/year

END OF EXAMPLE III-1

3.2.2 Single Event Sediment Loads

Soil erosion is governed by two processes: detachment of soil fines and transport of soil fines to the receiving water body. Detachment of soil fines can be accomplished by erosive rainfall or by shear forces at the soil surface created by surface runoff. One of the shortcomings of the USLE is that it does not explicitly consider transport nor detachment by runoff. Williams (1975) modified the USLE by replacing the "R" factor with a "runoff energy" factor to provide more accurate sediment loss prediction for single storm events. In addition this modification eliminates the need for the sediment delivery ratio. The form of this modification is

$$Y(S)_E = 95\ (Vq_p)^{0.56}\ KLSCP \tag{III-3}$$

where

$Y(S)_E$ = sediment yield in tons per event
V = volume of runoff in acre-feet and
q_p = peak flow rate in cubic feet per second

Other terms are as previously defined.

Alternatively the modified USLE (MUSLE) can be expressed in metric units as

$$Y(S)_E = 11.8\ (Vq_p)^{0.56}\ KLSCP \tag{III-4}$$

where

$Y(S)_E$ = sediment yield in tonnes
V = volume of runoff (m^3)and
q_p = peak runoff rate (m^3/sec)

In order to use MUSLE the terms V and q_p must be evaluated. This is most conveniently accomplished using the Soil Conservation Service runoff curve number method (Mockus, 1972).

3.2.2.1 Evaluation of Total Storm Runoff

The depth of runoff from the watershed area is estimated by the following Equation:

$$Q = (R-0.2S)^2/(R+0.8S) \tag{III-5}$$

where

Q = the depth of runoff from the watershed area (in, cm)
R = the total storm rainfall (in, cm) and
S = water retention parameter (in, cm)

The storm runoff volume can be calculated by

$$V = a\ A_w Q \tag{III-6}$$

where

V = total storm runoff volume (acre-ft, m^3)
a = a units conversion,0.083 English, 100 metric
A_w = watershed area (acres, ha)
Q = depth of runoff (in, cm)

S, the watershed retention parameter, is calculated using

$$S = \left(\frac{1000}{CN} - 10\right) \cdot a \tag{III-7}$$

where

CN = the SCS Runoff Curve Number (dimensionless) and
a = 1.0 English, 2.54 metric.

Runoff curve numbers are dependent upon antecedent soil water conditions, the relative permeability of the soil and vegetation cover and management factors. Table III-9 gives runoff curve numbers for various combinations of the above factors. The table is used by first determining the hydrologic soil group. Descriptions of each group are located at the bottom of the table. Next, move to the proper row for the crop/management scheme. Within each crop/management scheme a subrow labeled Hydrologic Condition is found. The qualifiers "good", "fair", or "poor" indicate relative management conditions. For instance, under the crop management scenario "small grains", "contoured", a "poor" hydrologic condition would be a poor stand of vegetation with breakthroughs in the contours both of which would increase surface runoff.

TABLE III-9

RUNOFF CURVE NUBERS FOR HYDROLOGIC SOIL-COVER COMPLEXES (FOR ANTECEDENT RAINFALL CONDITION II)

Land Use or Cover	Treatment or Practice	Hydrologic Condition	Hydrologic Soil Group*			
			A	B	C	D
Fallow	Straight row	--	77	86	91	94
Row crops	Straight row	Poor	72	81	88	91
	Straight row	Good	67	78	85	89
	Contoured	Poor	70	79	84	88
	Contoured	Good	65	75	82	86
	Terraced	Poor	66	74	80	82
	Terraced	Good	62	71	78	81
Small grain	Straight row	Poor	65	76	84	88
	Straight row	Good	63	75	83	87
	Contoured	Poor	63	74	82	85
	Contoured	Good	61	73	81	84
	Terraced	Poor	61	72	79	82
	Terraced	Good	59	70	78	81
Close-seeded legumes or rotation meadow	Straight row	Poor	66	77	85	89
	Straight row	Good	58	72	81	85
	Contoured	Poor	64	75	83	85
	Contoured	Good	55	69	78	83
	Terraced	Poor	63	73	80	83
	Terraced	Good	51	67	76	80
Pasture or range		Poor	68	79	86	89
		Fair	49	69	79	84
		Good	39	61	74	80
	Contoured	Poor	47	67	81	88
	Contoured	Fair	25	59	75	83
	Contoured	Good	6	35	70	79
Meadow (permanent)		Good	30	58	71	78
Woods (farm woodlots)		Poor	45	66	77	83
		Fair	36	60	73	79
		Good	25	55	70	77
Farmsteads		--	59	74	82	86
Roads and right-of-way (hard surface).		--	74	84	90	92

*Soil Group	Description
A	Lowest Runoff Potential: Includes deep sands with very little silt and clay, also deep, rapidly permeable loess.
B	Moderately Low Runoff Potential: Mostely sandy soils less deep than A, and loess less deep or less aggregated than A, but the group as a whole has above-average infiltration after thorough wetting.
C	Moderately High Runoff Potential: Comprises shallow soils and soils containing considerable clay and colloids, though less than those of group D. The group has below-average infiltration after presaturation.
D	Highest Runoff Potential: Includes mostly clays of high swelling per cent, but the group also includes some shallow soils with nearly impermeable subhorizons near the surface.

Source: Schwab *et al.*, 1966

The intersection of the crop/management/condition row with the hydrologic soil group column is the curve number for this watershed. This table is, however, for antecedent soil moisture condition II. To account for very wet or very dry antecedent conditions the curve number is multiplied by the appropriate correction found in Table III-10.

3.2.2.2 Estimation of Peak Storm Runoff

In order to estimate peak storm runoff a hydrograph shape must be assumed. Commonly, a triangular or trapezoidal shape is used. A trapezoidal hydrograph is used here. The equation for the peak runoff rate is

$$q_p = \frac{a\,A_w\,R\,Q}{T_r\,(R-0.2S)} \qquad \text{(III-8)}$$

where

q_p = the peak runoff rate (ft^3/sec, m^3/sec)
A_w = watershed area (acres, ha)
R = total storm rainfall (in, cm)
Q = storm runoff depth (in, cm)
Tr = storm duration (hr)
a = a units conversion constant 1.01 English, 0.028 metric.

For the development of the above equation see Haith (1980).

EXAMPLE III-2

Assessing Single Event Sediment Loads and Storm Runoff

The 180 acres (72.8 ha) of cropland in the previous example will be considered here. The USLE parameters are the same. Assume a 4.5 cm rain falls in a 3 hour period in early June. The soil hydrologic condition is good and the soils are in hydrologic group A. This particular storm was preceded by 4 cm (1.6 in) in the previous five-day period. Calculate total storm runoff and sediment yield.

TABLE III-10

ANTECEDENT RAINFALL CONDITIONS AND CURVE NUMBERS (FOR $I_a = 0.2S$)

Curve Number of Condition II	Factor to Convert Curve Number for Condition II to Condition I	Factor to Convert Curve Number for Condition II to Condition III
10	0.40	2.22
20	0.45	1.85
30	0.50	1.67
40	0.55	1.50
50	0.62	1.40
60	0.67	1.30
70	0.73	1.21
80	0.79	1.14
90	0.87	1.07
100	1.00	1.00

Condition	General Description	5-Day Antecedent Rainfall in inches: Dormant Season	5-Day Antecedent Rainfall in inches: Growing Season
I	Optimum soil condition from about lower plastic limit to wilting point	<0.5	<1.4
II	Average value for annual floods	0.5-1.1	1.4-2.1
III	Heavy rainfall or light rainfall and low temperature within 5 day prior to the given storm	>1.1	>2.1

Source: Schwab _et_. _al_., 1966

Solution:

First the total storm runoff volume will be estimated. The curve number from Table III-9 is (row crops, contoured, good, A) 65 since antecedent rainfall (growing season) is between 1.4 and 2.1 inches the antecedent condition is II and no correction is needed. Therefore using Equation III-7,

$$S = \left(\frac{1000}{65} - 10\right) \cdot 2.54 = 13.68$$

Using Equation III-5

$$Q = [4.5 - 0.2\ (13.68)]^2/[4.5 + 0.8\ (13.68)]$$
$$= 0.20$$

The storm runoff volume is (Eqn. III-6)

$$V = 100\ (72.8)\ (.2)$$
$$= 1456\ m^3$$

Now the peak runoff is estimated from Equation III-8

$$q_p = \frac{0.028\ (72.8)\ (4.5)\ (0.20)}{(3)\ [4.5 - 0.2\ (13.68)]}$$
$$= 0.35\ m^3/sec$$

The watershed sediment yield for the storm is (Eqn. III-4)

$$Y(S)_E = 11.8\ [1456\ (.35)]^{0.56}\ (.37)\ (1.08)\ (.49)\ (.60)$$
$$= 45.5 \text{ tonnes - sediment}$$

END OF EXAMPLE III-2

3.2.3 NITROGEN LOADING FUNCTION

While the complex interactions in soil, air, water and plants are reasonably well understood, methods for quantifying movements within the system are still in the research stage. Methods which are suitable for general use often oversimplify the problem. They must be used with discretion and may be inadequate in certain cases. For instance, it is not presently possible to describe leaching processes for soluble forms of nitrogen in a simplified manner. The nitrogen loading function assumes that erosion is the primary N source for cultivated land. The loading functions exclude leaching losses, and predict the amount of total nitrogen that is released to surface waters by runoff and erosion. For predicting N and P loads from forested areas see Section 3.2.7.

3.2.3.1 Nitrogen Loading Function for Erosion Loss

The nitrogen loading due to erosion is computed as:

$$Y(NT)_E = a \cdot Y(S)_E \cdot C_S(NT) \cdot r_N \qquad \text{(III-9)}$$

where

$Y(NT)_E$ = total nitrogen loading due to erosion, (kg/yr or event, lb/year or event)

a = dimensional constant (10 for metric units, 20 for English units)

$C_S(NT)$ = total nitrogen concentration in soil, g/100 g

$Y(S)_E$ = sediment loading from surface erosion, (MT/year or event, tons/year or event)

r_N = nitrogen enrichment ratio

Available nitrogen can be obtained by using a fraction f_N which is the ratio of available N to total N loss predicted by erosion. Thus, the available nitrogen load is

$$Y(NA)_E = Y(NT)_E \cdot f_N \qquad \text{(III-10)}$$

3.2.3.2 Evaluation of Parameters in the Nitrogen Loading Function

In the erosion nitrogen loading function three parameters must be evaluated. The value of $Y(S)_E$ comes from the USLE or MUSLE depending upon whether long term or single event-loads are being estimated.

Values of the nitrogen enrichment ratio r_N are shown in Table III-12. These values range from roughly 2.0 to 5.0. It is generally higher on sandy soils and lower on finely divided highly erodible soils. The enrichment ratio represents the effects of several processes which cause the nitrogen content of the eroded soil to be higher than the source soil back in the watershed. This is mainly due to preferential detachment and transport of smaller soil particles which have higher N associated with them.

The user may want to use a low and a high value for r_N to evaluate a range of erosion nitrogen losses. The enrichment ratio is quite variable with regard to management practices even for the same soil type.

The enrichment ratio also varies from storm to storm and within storms. Menzel (1980) found that r_N varied logarithmically with sediment loss. His equation is

$$\ln [r_N] = 2.0 + 0.20 \ln[Y(S)_E] \qquad \text{(III-11)}$$

where

Y is the sediment loss in (Kg/ha).

This equation can be used only on a per event basis.

The value of $C_S(NT)$ in the plowed layer of soil is variable from location to location and from season to season. Estimates of native soil nitrogen in the U.S. indicate a range between 0.02 and 0.4 percent (Jenny, 1930). Parker *et at*. (1946) published a map showing the nitrogen content in the top 1-ft layer in the U.S. (Figure III-10). Data in this figure

TABLE III-12

ENRICHMENT RATIOS FOR NITROGEN

Soil	Conditions	Slope	r_N	Reference
	Prevailing Practice		1.74	Stoltenburg & White (1953)
	Conservative Practice		2.08	
Collington	Control, Total N	3.5%	3.88	Knoblauch, Koloday and Brill (1942)
Sandy Loam	Cover crop		4.09	
	Manure		4.28	
	Cover & manure		3.35	
	Total N		5.0	Neal (1944)
Almena Silt Loam	Total N	3.0%	1.34	Massey, Jackson & Hays (1953)
Fayette silt Loam	Total N	11.0%	1.08	
Silt loam soils			2.7	Massey & Jackson (1952)

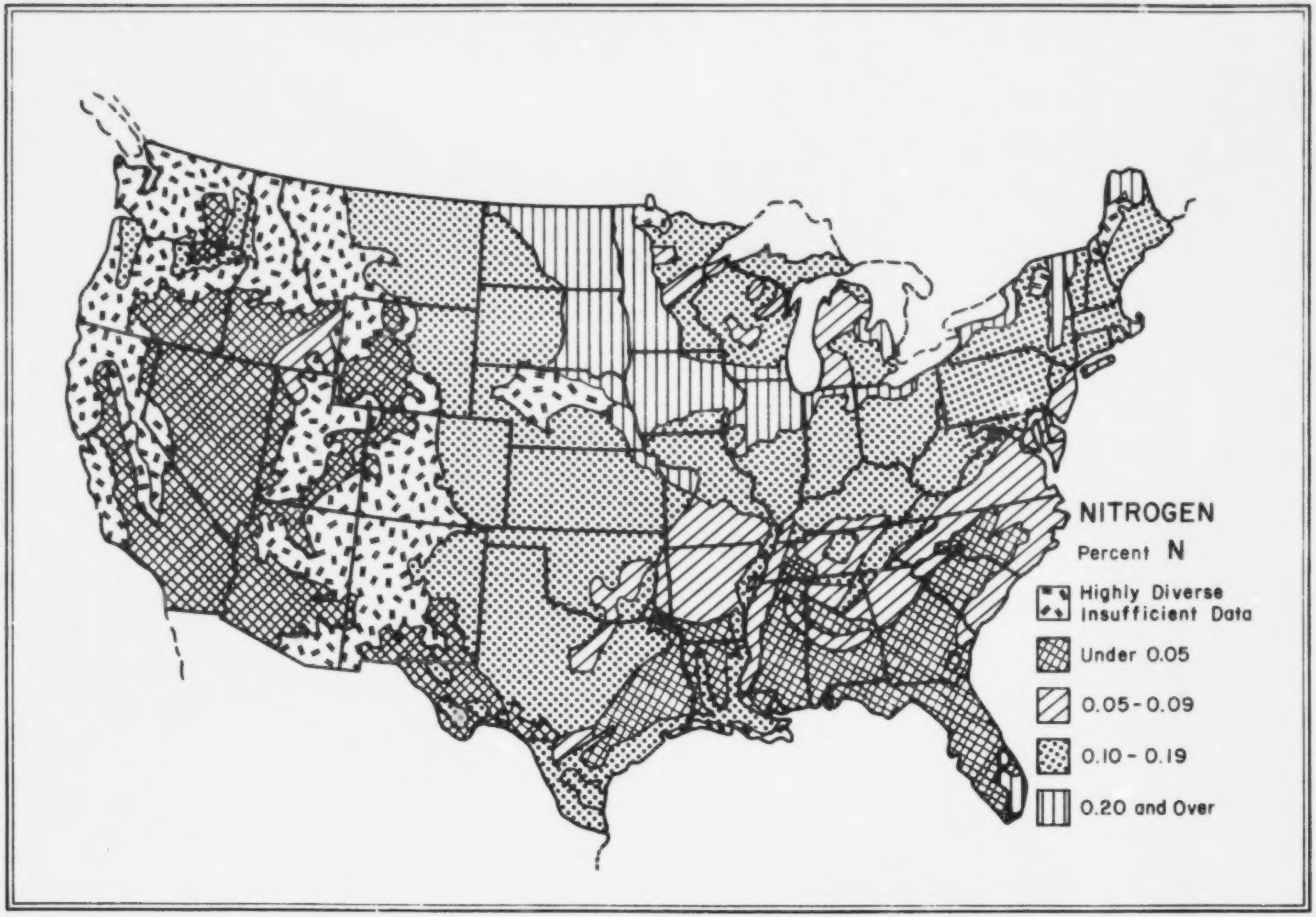
NITROGEN
Percent N
Highly Diverse Insufficient Data
Under 0.05
0.05-0.09
0.10-0.19
0.20 and Over

FIGURE III-10 PERCENTAGE NITROGEN (N) IN SURFACE FOOT OF SOIL (PARKER, ET AL., 1946)

should be viewed in general terms; for specific sites, local sources such as ASCS and SCS Soil Survey should be consulted.

Precipitation also contributes to the soil nitrogen. Atmospheric nitrogen extracted by soil microbes becomes incorporated into soil organic matter. Animal manures, crop residues, and other wastes contribute significant amounts of nitrogen to the soil. Jenny (1930) expressed the nitrogen content of the soil in terms of temperature, T, and a humidity factor, H. Jenny's equation is:

$$C_S(NT) = 0.55_e{}^{-0.08T}\,(1-e^{-0.005H}) \qquad \text{(III-12)}$$

$$H = \frac{P}{(1 - \frac{RH}{100})\ SVP_t} \qquad \text{(III-13)}$$

where

P = precipitation, mm/year

$C_S(NT)$ = concentration of soil nitrogen, g/100 g

T = annual average temperature, ^oC

RH = relative humidity, percent

SVP_t = saturated vapor pressure at given temperature, mm of Hg

Equation III-14 shows the relation between SVP_t and T (Gladstone, 1946).

$$SVP_t = 10\ \left[9.2992 - 2360/(273 + T)\right] \qquad \text{(III-14)}$$

The solution of Equation III-12 is shown graphically in Figure III-11. The value of humidity factor, H, can be determined from Equations III-13 and III-14. A nomograph solution of H is shown in Figure III-12. For given values of precipitation, relative humidity and temperature, the value of H can be quickly and accurately established from Figure III-12. For example, given P_1 = 500 mm/year (19.7 in/year), RH_1 = 60 percent, and T_1 = 5 ^oC (41 ^oF), the value of H factor can be determined as follows: using a straight-edge ruler, align P_1 and RH_1 to intersect on the index line at "A" as shown on the inset of Figure III-12. Align "a" with T_1 on the

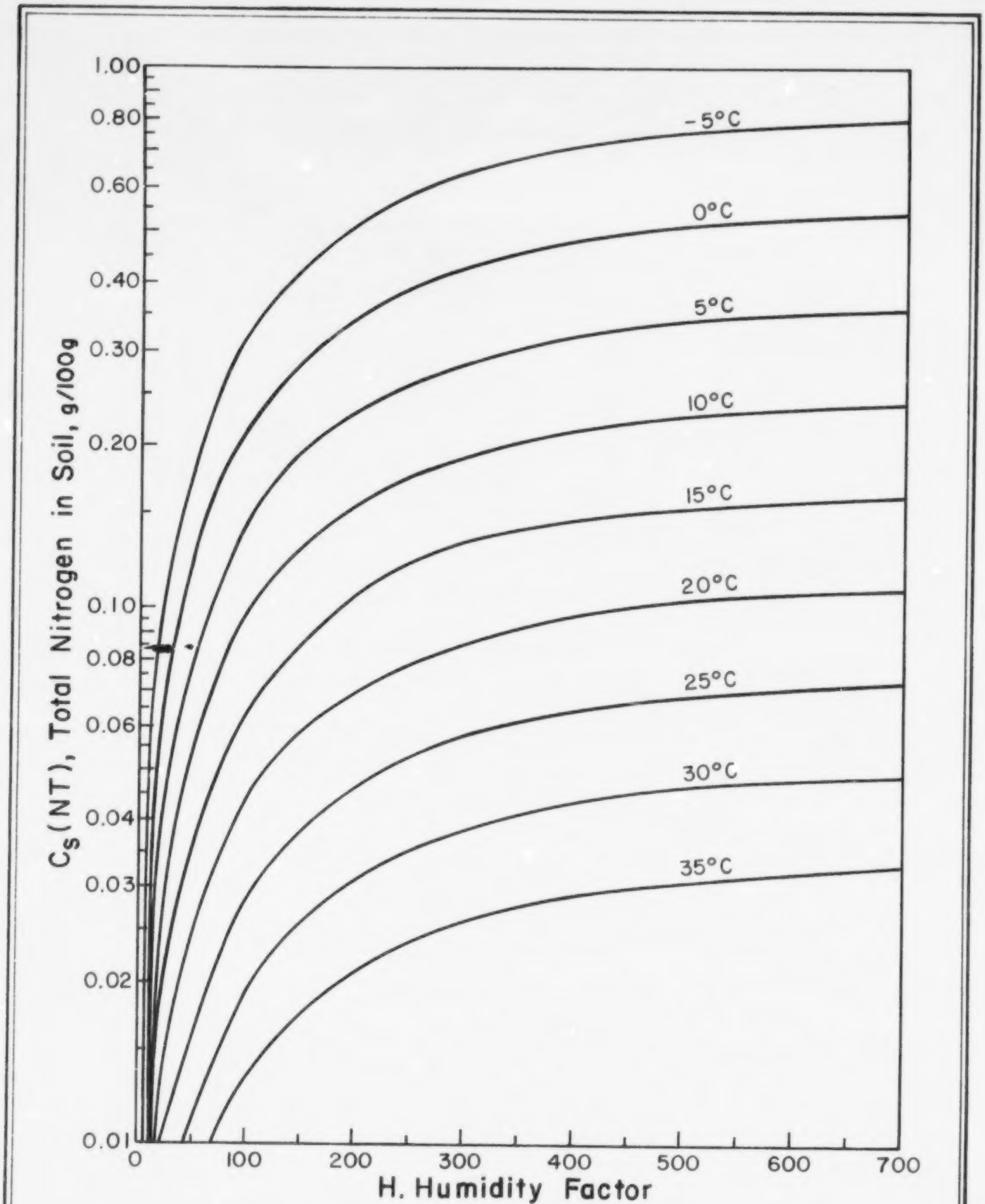

FIGURE III-11 SOIL NITROGEN VS. HUMIDITY FACTOR AND TEMPERATURE

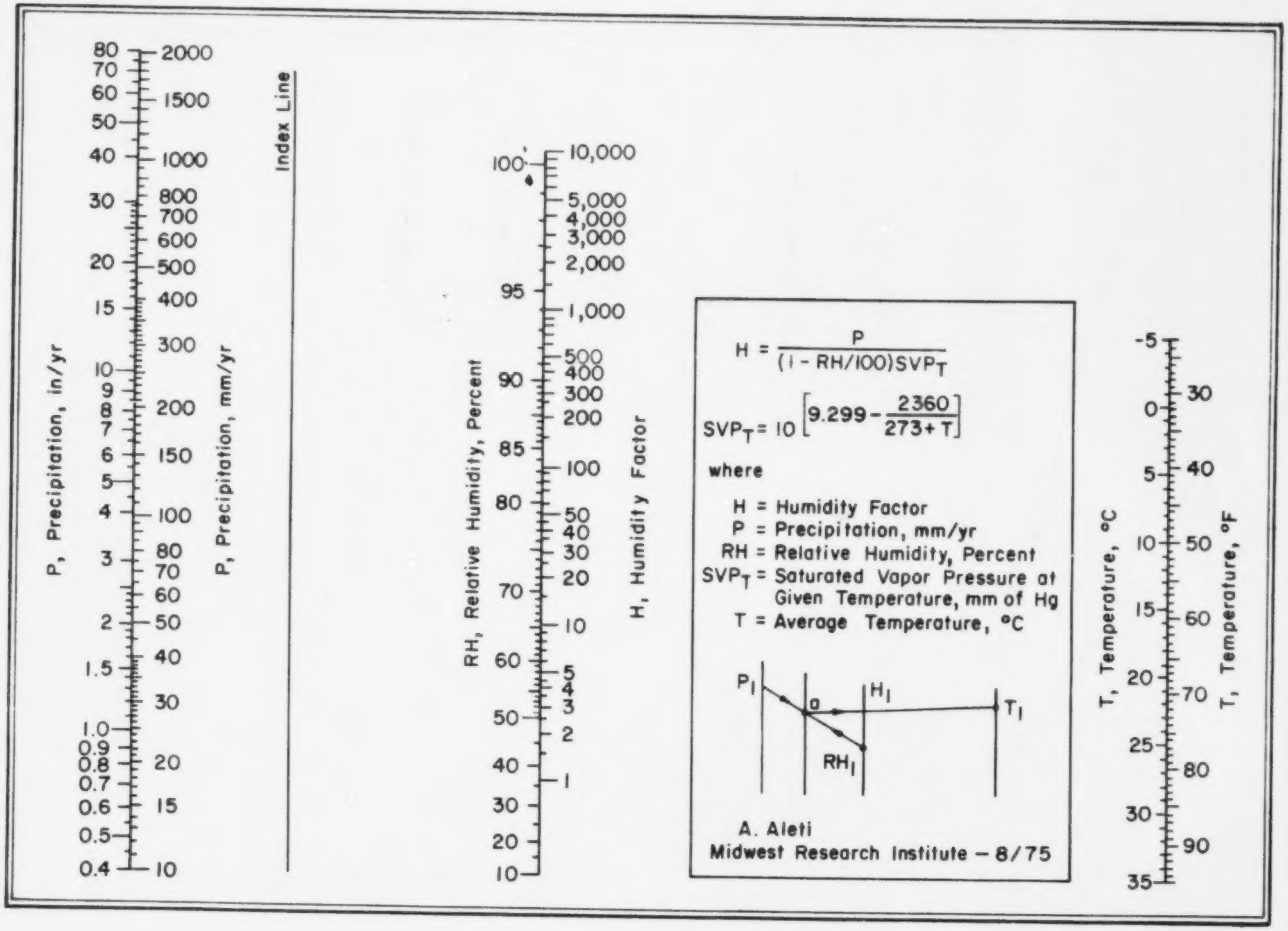
P, Precipitation, in/yr
80
70
60
50
40
30
20
15
10
9
8
7
6
5
4
3
2
1.5
1.0
0.9
0.8
0.7
0.6
0.5
0.4
P, Precipitation, mm/yr
2000
1500
1000
800
700
600
500
400
300
200
150
100
80
70
60
50
40
30
20
15
10
Index Line
RH, Relative Humidity, Percent
100
95
90
85
80
70
60
50
40
30
20
10
H, Humidity Factor
10,000
5,000
4,000
3,000
2,000
1,000
500
400
300
200
100
50
40
30
20
10
5
4
3
2
1
$H = \frac{P}{(1 - RH/100)SVP_T}$
$SVP_T = 10^{\left[9.299 - \frac{2360}{273+T}\right]}$
where
H = Humidity Factor
P = Precipitation, mm/yr
RH = Relative Humidity, Percent
SVP_T = Saturated Vapor Pressure at Given Temperature, mm of Hg
T = Average Temperature, °C
P_1
a
H_1
T_1
RH_1
A. Aleti
Midwest Research Institute – 8/75
T, Temperature, °C
-5
0
5
10
15
20
25
30
35
T, Temperature, °F
30
40
50
60
70
80
90

FIGURE III-12 NOMOGRAPH FOR HUMIDITY FACTOR, H

temperature scale to intersect the H scale. The result on the H scale is 194.

Data in Figure III-10 may be used as a check on current data. Equations III-12 and III-13 may be used to calculate nitrogen content of soil more precisely if necessary data are available for using these equations. Again data from State Agricultural Experiment Stations, and SCS Soil Surveys are much more dependable than the above equations and should be consulted whenever possible.

The fraction of available nitrogen (f_n) or that nitrogen which can be directly used by plants is usually considered to be the $NH_4^+ + NO_3^-$ fraction. The erosion nitrogen load which consists primarily of organic N bound in detritus does not necessarily correlate well with the NH_4^+ or NO_3^- load especially in areas with low surface runoff and sediment loss. Forms of nutrients on the watershed surface will vary with

1. amount and type of plant residue remaining in the field (Timmons et al., 1970)
2. land use (Logan, 1980)
3. application of manures and fertilizers (Reddy, 1980) and
4. type of tillage management (Frere, et al., 1980)

It is suggested for screening purposes that the user rely on total N load estimates.

3.2.4 PHOSPHORUS LOADING FUNCTION

Phosphorus occurs naturally in soil from weathering of primary phosphorus-bearing minerals in the parent material. Additions of plant residues and fertilizers by man enhances the phosphorus content of the surface soil layer.

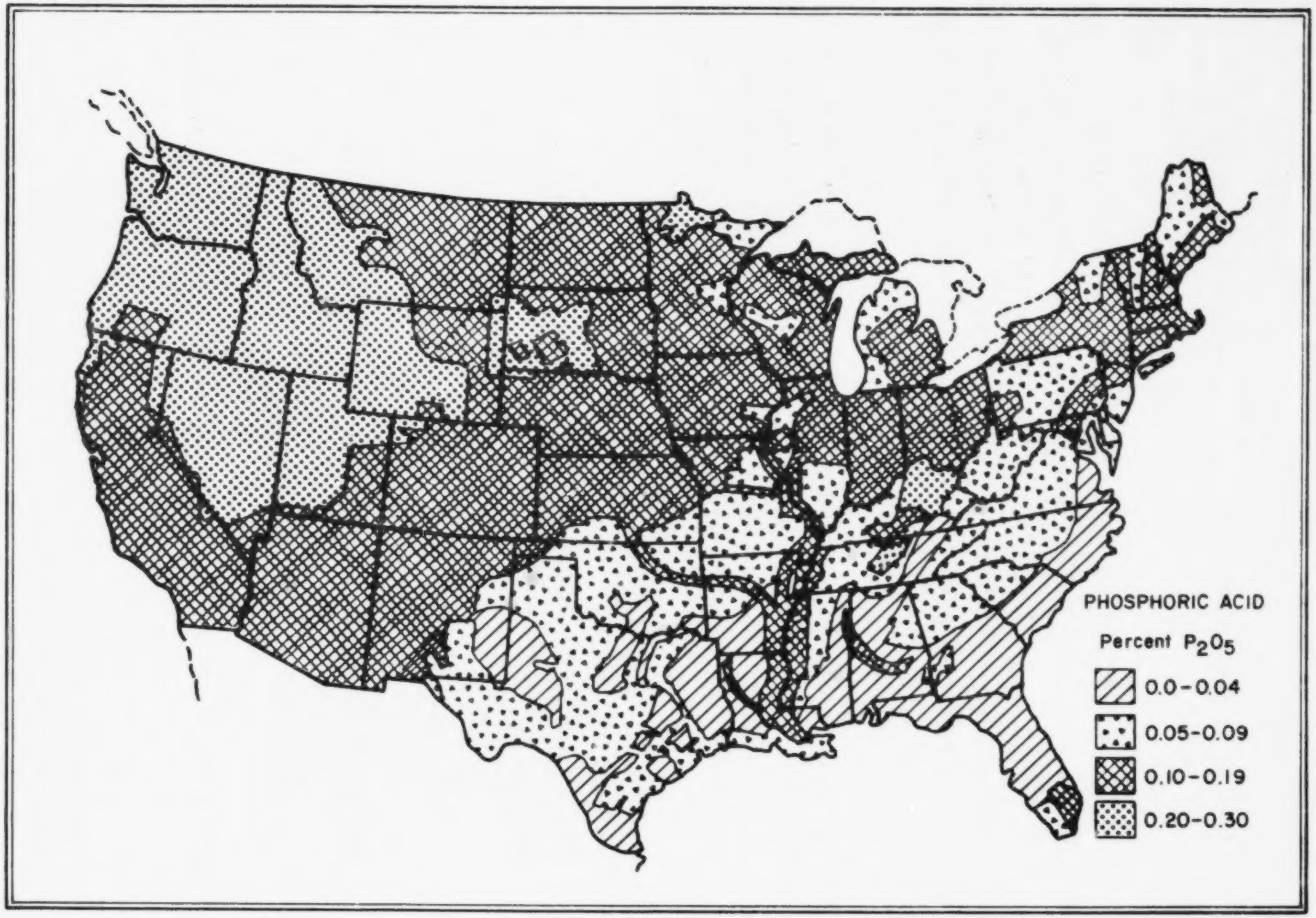
PHOSPHORIC ACID
Percent P_2O_5
0.0-0.04
0.05-0.09
0.10-0.19
0.20-0.30

FIGURE III-13 PHOSPHORUS CONTENT IN THE TOP 1 FT OF SOIL (PARKER, ET AL., 1946)

Phosphorus in soils occurs either as organic or inorganic phosphorus The relative proportion of phosphorus in these two categories varies widely. Organic phosphorus is generally high in surface soils where organic matter tends to accumulate. Inorganic forms are prevalent in subsoils. Soil phosphorus is readily immobilized due to its affinity to certain minerals. In strongly acid soils the formation of iron and aluminum phosphates, and in alkaline soils, the formation of tricalcium phosphate reduces the availability of soil phosphorus. Once it enters a stream, the partioning of phosphorus between the sediment and solution phases becomes significant in the nutrition of aquatic microorganisms.

Phosphorus transport from a given site to a stream can occur either by erosion or by leaching. The predominant mode of transport is via soil erosion. The soil solution usually contains less than 0.1 μg of phosphorus per milliliter; the leaching losses are thus extremely low even in well-drained soils. Exceptions are sands and peats which have little tendency to react with phosphorus.

The loading function for phosphorus is based on the soil erosion mechanism. The loading function is:

$$Y(PT) = a \cdot Y(S)_E \cdot C_S(PT) \cdot r_p \qquad \text{(III-15)}$$

where

$Y(PT)$ = total phosphorus loading, (kg/year, lb/year)
a = a dimensional constant (10 metric, 20 English)
$Y(S)_E$ = sediment loading, (MT/year, tons/year)
$C_S(PT)$ = total phosphorus concentration in soil, g/100 g
r_p = phosphorus enrichment ratio

Available phosphorus may be computed as in Equation III-11:

$$Y(PA) = Y(PT) \cdot f_p \qquad \text{(III-16)}$$

where

$Y(PA)$ = yield of available phosphorus, (kg/year, lb/year)

f_p = ratio of available phosphorus to total phosphorus

3.2.4.1 Evaluation of Parameters in the Phosphorus Loading Function

As with the nitrogen erosion loading equation two parameters must be evaluated - the soil concentration of total P and the phosphorus enrichment ratio. The sediment load, $Y(S)_E$, is known from previous analysis.

Local sources should be consulted in preference to using the estimates of $C_S(PT)$ in Figure III-13. The Soil Conservation Service or agriculture extension personnel will be the best sources of this information.

Table III-13 shows enrichment ratios for phosphorus found in the literature. On the whole r_p is slightly less than r_N having values of about 1.0 to 4.0. Sharpley (1980) and Menzel (1980) have both used equations of the form

$$\ln[r_p] = a + b \ln [Y(S)_E] \qquad \text{(III-17)}$$

where

$a = 2.48$ (Sharpley, 1980)

$b = 0.27$ and

$a = 2.0$ Menzel (1980)

$b = 0.20$

to predict enrichment ratios for individual storm events.

As with nitrogen the available to total P ratio varies with soil type, crop type and management practice. Users should use total P in subsequent analyses whenever possible.

TABLE III-13

ENRICHMENT RATIOS FOR PHOSPHORUS

Soils	Conditions	Slope	r_p	Reference
	Prevailing Practice		1.82	Stoltenberg & White (1953)
	Conservative Practice		2.03	
Collington	Check plot	3.5%	1.59	Knoblauch, Koloday & Brill (1942)
Sandy	Cover crop		1.56	
Loam	Manure		1.47	
	Manure & cover crop		1.47	
	Total P		3.1	Neal (1941)
	Available P		0.99	
Almena silt loam	Available P corn oats of a corn-oats hay-hay rotation	3.0	1.92	Massey, Jackson & Hays (1953)
Fayette silt loam	Available P	11.0%	2.20	
Dunmore silt loam	Available P Wheat dilute H_2SO_4 soluble	5-25%	3.74	Rogers (1941)
	Available P Corn		1.79	
	Available P		3.4	Massey & Jackson 1952

Schuman, et al. (1970) have reported an empirical relation between sediment phosphorus (concentration in ppm, C_S(PT) and soluble phosphorus (concentration in ppm, C_Q(P)) for Iowa soils. The relation may be stated as:

$$C_Q(P) = a + b \cdot C_S(PT) \qquad \text{(III-18)}$$

where a and b are regression coefficients. The reported values of a and b are 0.018 and 0.047, repectively. Equation III-18 shows that the ratio of solution phosphorus to sediment phosphorus is just under 1 to 20.

Taylor (1967) suggested that about 10 percent of the total phosphorus in eroded soil is ordinarily available for aquatic plant growth. However, some values as high as 20 to 30 percent have been suggested.

3.2.5 Organic Matter Loading Function

The loading function is:

$$Y(OM)_E = a \cdot C_S(OM) \cdot Y(S)_E \cdot r_{OM} \qquad \text{(III-19)}$$

where

$Y(OM)_E$ = organic loading, (kg/year, lb/year)
a = a dimensional constant (10 metric, 20 English)
$C_S(OM)$ = organic matter concentration of soil, g/100 g
$Y(S)_E$ = sediment loading, (MT/year, tons/year)
r_{OM} = enrichment ratio for organic matter in eroded soil

3.2.5.1 Evaluation of Parameters in the Organic Matter Loading Function

The value of $Y(S)_E$ can be obtained from procedures discussed previously. The value of $C_S(OM)$ should be obtained preferably from current or historical data for a given area, (e.g. from the extension service). For approximate values, $C_S(OM)$ may be taken as equal to 20 x $C_S(NT)$, where

$C_S(NT)$ is the total nitrogen concentration in the soil (Buckman and Brady, 1969).

The enrichment ratio for organic matter r_{OM} has a range of 1 to 5 being higher on sandy soils and lowest on finely divided highly erodible mineral soil (McElroy et al., 1976). Foster (1980) gives a range of r_{OM} of 1.2 to 4.4. Frequently it is assumed that r_{OM} is that of the clay enrichment ratio. The data of Leonard et al. (1979) show that this was approximately the case for four watersheds in the Piedmont region of Georgia. Enrichment rations for organic matter found in the literature are shown in Table III-14.

Obviously, the effects of management practices can be pronounced on r_{OM}. One would expect higher r_{OM} with practices such as residue cover and slope reduction. In general, practices which reduce runoff velocities and rainfall detachment probably increase r_{OM}.

EXAMPLE III-3

Example of Loading Computation for Nitrogen, Phosphorus, Organic Matter

The watershed used in Example III-1 (Section 3.2.4) for Parke County in Indiana will be used to illustrate the methodology presented in this section for computing pollutant loads. Computation of available nitrogen, available phosphorus, and organic matter annual loads is required:

The following data, plus soils data, are required:

Soil nitrogen content.
Soil phosphorus content.

The preferred source of data is local records. Jenny's equation (Equation. III-12) and Figure III-13 are alternate sources from which general values may be estimated.

TABLE III-14

ENRICHMENT RATIOS FOR ORGANIC MATTER IN SURFACE RUNOFF

Soil	Conditions	Slope	r_{om}	Reference
Collington Sandy Loam	Check plot	3.5%	4.13	Knoblauch, Koloday and Brill (1942)
	Cover crop		4.48	
	Manure		4.23	
	Cover + manure		3.97	
	Prevailing Practice		1.24	Staltenberg & White (1953)
	Conservation Practice		1.38	
			4.7	Neal (1944)
Almena Silt Loam	Corn oats of a corn oats-hay-hay rotation	3%	4.6	Massey, Jackson & Hays (1953)
Fayette Silt Loam	Corn oats of a corn oats-hay-hay rotation	11%	1.24	
Silt Loam Soils			1.15	Massey & Jackson (1952)
Sandy Loam Soils	Contoured (P1)	2-5%	2.6	Leonard, Langdale & Fleming (1979)
	Countoured (P2)	2-4%	2.1	
	Terraced w/grassed (P3) Waterway	1-2%	2.4	
	Terraced w/grassed (P4) Waterway	1-2%	1.9	

* Values are averages for 4, 1, 3 and 1 summer storm(s) respectively for P1, P2, P3, P4 watersheds.

Nitrogen Loading

Using the following data, soil nitrogen content is calculated:

Average annual temperature = 10^oC
Average annual precipitation = 96.5 cm
Average annual relative humidity = 70 percent

Using the nomograph given in Figure III-12, the value of the H factor is determined to be 350. From Figure III-11, and using H = 350 and T = 10^oC, the value of $C_S(NT)$, the soil nitrogen content is estimated to be 0.204 percent or 0.204 g/100 g. Using Equations III-9 and III-10 and r_N = 2.0,

$$\begin{aligned} Y(NA)_E &= 20 \cdot Y(S)_E \; 0.2 \cdot 2.0 \\ &= 8 \cdot Y(S)_E \end{aligned}$$

The values of areal sediment yield as given in Example III-1 are shown below in Table III-15.

Phosphorus Loading

Assuming $C_S(PT)$ = 0.15 g/100 g for the area and r_p = 1.5, equation III-10 gives

$$\begin{aligned} Y(PA)_E &= 20 \cdot Y(S)_E \cdot 0.15 \cdot 1.5 \\ &= 4.5 \; Y(S)_E \end{aligned}$$

Organic Matter Loading

Using Equation III-19, data for $C_S(OM)$, $Y(S)_E$, r_{OM} are needed.

Assume that the value of $C_S(OM)/C_S(NT)$ equals 20 and r_{OM} =2.5,

TABLE III-15

CALCULATED SEDIMENT, NITROGEN, PHOSPHORUS AND ORGANIC MATTER LOADS FOR PARKE CO., INDIANA WATERSHED

	Load (tons/year)			
Land Use	Sediment	Total Nitrogen	Total Phosphorus	Organic Matter
Cropland	2530	10.1	5.7	253
Pasture	121	0.5	0.3	12
Woodland	430	1.7	1.0	43
Total	2797	12.3	7.0	308

$$Y(OM)_E = 20 \cdot 2.5 \cdot Y(S)_E \cdot 20 \cdot C_S(NT)$$
$$= 1000 \cdot C_S(NT) \cdot Y(S)_E$$

Using $C_S(NT) = 0.2$ percent,

$$Y(OM)_E = 200\ Y(S)_E$$

The values for nitrogen, phosphorus organic matter loading are also presented in Table III-15.

END OF EXAMPLE III-3

3.2.6 Accuracy of Nutrient and Organic Matter Loadings from Erosion

The accuracy of a prediction using loading functions depends upon the accuracy in predicting sediment loading, watershed concentration (or availability) of a pollutant, and its enrichment in eroded sediments.

Predicting sediment loss has been and continues to be a problem in both hand calculation methods and computer models. Prediction of sediment loads is generally better for longer periods; that is, annual predictions are better than seasonal predictions which are better than for single storm events. Storm event sediment loads are particularly a problem for hand calculation methods such as the USLE but the use of MUSLE improves the accuracy.

Aside from sediment load prediction, the dynamic surface concentration of nutrient forms is also difficult to estimate unless computer simulation techniques are used. Frere et al. (1980) have indicated that typical values for soil nitrogen and phosphorus vary from 6 to 10 fold.

Since most enrichment ratios observed for organic matter, N and P have values between 1 and 5, their estimation seems the least critical of the three parameters of the loading function.

Total nutrient losses for N and P are among the most accurate for agricultural watersheds. This is primarily because most of the N lost is organic which is bound to fines or is itself detrital. Similarly, P is mostly particulate in cultivated watersheds. The prediction of individual forms of either N or P is less accurate because of the chemical transformation which must be considered and is impractical using hand calculator methods.

Table 16 shows the percentage of explained variance for several parameters by regression on suspended solids from several different parts of the country. The information is only for regressions which were linear with respect to both the independent and dependent variables. As expected, TKN and Total P are among the highest, with explained variance decreasing for more weakly adsorbed constituents.

3.2.7 Nitrogen and Phosphorus Loading From Forested Watersheds

Because of the protection of the soil surface afforded by tree canopy and tree litter in forested watersheds, the quantity of soil eroded from the watershed surface is generally small. Contrast the two order of magnitude differences in sediment loading between cropland and woodland computed in Example III-1. Hence the mechanism by which nutrients are lost from these watersheds are quite different from those erosion mechanisms which operate in agricultural watersheds. For this reason the erosion loading equations are not recommended for use in forested systems.

An empirical procedure is given below for estimating N outputs for forested basins based on precipitation input load. The equation is

$$Y(N)_F = A \cdot N_{pr} \cdot b \qquad \text{(III-20)}$$

TABLE III-16

VARIATION IN CONSTITUENT ACCOUNTED FOR BY REGRESSION ON SUSPENDED SOLIDS (Linear Models Only)

Constituent	Data Base	% Explained Variance
Nutrients		
TKN	Watkinsville, GA	37.1
	Buffalo Bill, IO	11.1
	Michigan State, MI	2.1
	Honey Creek, OH	19.4
Total P	Watkinsville	18.7
	Honey Creek	67.9
$PO_4^{\equiv}$-P	Watkinsville	6.9
	Buffalo Bill	5.6
NH_4^+-N	Watkinsville	18.5
	Buffalo Bill	15.0
	Michigan State	5.8
NO_3^--N	Buffalo Bill	13.8
	Michigan State	0.06
Miscellaneous		
BOD	Buffalo Bill	32.0
Iron	Honey Creek	82.8

Source: Zison, 1980

where

$Y(N)_F$ = the loading of N from a forested watershed (Kg, lb)
A = the watershed area (ha, acres)
N = the input precipitation nitrogen load (kg/ha, lb/acre) and
b = an attenuation factor

An alternative form of Equation III-20 is

$$Y(N)_F = A \cdot C(N)_{Pr} \cdot Q(Pr) \cdot b \cdot a \tag{III-21}$$

where

$C(N)_{pr}$ = a typical N concentration in precipitation (mg/l)
$Q(Pr)$ = the depth of rainfall over the period (in, cm) and
a = a units conversion factor
= 0.23 English units
= 0.10 metric units

Equation III-21 should be used if local and reliable N precipitation concentration data are available. If not Equation III-20 can be used. The map in Figure III-14 or the data in Table III-17 can be used to estimate N_{pr} in this case.

The attenuation factor 'b' can be estimated using Table III-18. On the average the attenuation factors for N and P are 0.40 and 0.78 respectively. The attenuation factors are calculated from the data in Likens, et al., 1977.

3.2.8 Loading Values for Salinity Loads in Irrigation Return Flow

Perhaps the most useful method of establishing salinity loads is through loading values determined for particular regions. Lists of such values are presented in Tables III-19 through III-23 for subbasins in the Colorado River basin, and for irrigated regions in California.

Studies in the Twin Falls area and the Colorado River basin indicate that the range of values for salt pickup from irrigated lands is roughly 1.3 to 22 MT/ha/year (0.5 to 8 tons/acre/year) (Skogerboe and Law, 1971). These

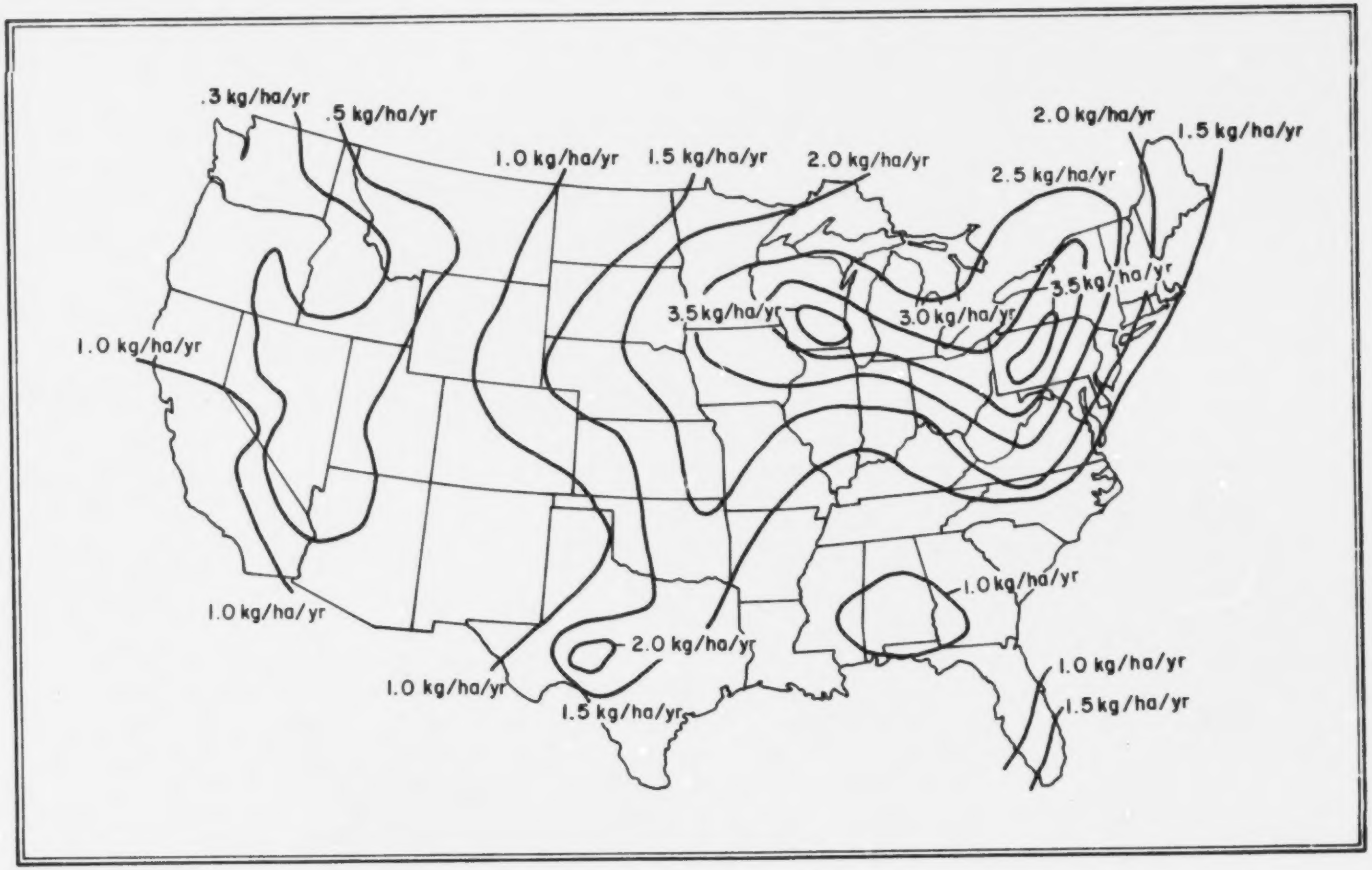
.3 kg/ha/yr
.5 kg/ha/yr
1.0 kg/ha/yr
1.5 kg/ha/yr
2.0 kg/ha/yr
2.0 kg/ha/yr
1.5 kg/ha/yr
2.5 kg/ha/yr
3.5 kg/ha/yr
3.5 kg/ha/yr
3.0 kg/ha/yr
1.0 kg/ha/yr
1.0 kg/ha/yr
1.0 kg/ha/yr
2.0 kg/ha/yr
1.0 kg/ha/yr
1.5 kg/ha/yr
1.0 kg/ha/yr
1.5 kg/ha/yr

FIGURE III-14 NITROGEN (NH_4-N AND NO_3-N) IN PRECIPITATION, (PERSONAL COMMUNICATION WITH MRI, J.H. CRAVENS, REGIONAL FORESTER, U.S.D.A.-FS EASTERN REGION, 1974)

TABLE III-17

ATMOSPHERIC CONTRIBUTIONS OF NITROGEN AND PHOSPHORUS IN RAINFALL

	N Contribution in Kg/ha/yr				P Contribution in Kg/ha/yr			
	NO_3-N+NH_4-N		Total N		Inorganic P		Total P	
	Low	High	Low	High	Low	High	Low	High
Northeastern U.S.	5.7	12.1	5.7	12.1	-	-	-	-
Southeastern U.S.	1.5	12.3	-	-	-	-	-	-
Midwestern U.S.	0.2	20.9	1.7	20.9	-	-	-	-
West/Southwestern U.S.	1.7	5.7	9.0	14.6	-	-	-	-
United States	-	-	-	-	0.18	0.18	0.08	0.80

Source: Weiner, et al. (1976)

TABLE III-18

NUTRIENT BUDGETS FOR VARIOUS TERRESTRIAL ECOSYSTEMS OF THE WORLD (kg/ha•yr)

	Location	Precipitation Input	Stream-water output	Net gain or loss	Annual precipitation, cm	Dominant vegetation[b]	Geology[c]	Attenuation Factor (b)
			Phosphorus					
Temperate: mostly angiosperm and deciduous forest	Coshocton, OH, U.S.	0.18[n]	0.05	+0.13	89	L, Pin	S_{shr} S_{cr} S_s	.27
	Hubbard Brook, U.S.	0.036	0.019	+0.017	130	Ac, F, B	I_{gr} M_{sh}	.53
	Pago Catchment, Australia	0.33	0.26	+0.07	150	E	M_{shr} I_g	.79
	Silverstream, New Zealand	0.2	0.03	+0.2	135	N	S_{sr} S_{shr} M_{sr} M_{sh}	.15
	Taughannock Creek, NY, U.S.	0.07	0.20	-0.13	96	Ac, Ti, Ts	S_{shr} S_c	2.85
	Walker Branch, TE, U.S.	0.54	0.02	+0.52	155	Q, C	S_c	.04 Avg. .77
Temperate: mostly coniferous and evergreen forest	Blue Range Catchment, Australia	0.39	0.42	-0.03	132	Pin	I_{gr} M_{sh}	.93
	Boundary Waters Canoe Area, MIN, U.S. (24)	0.14	0.015	+0.13	70	Pin, Pic, B	I_{gr} S_{sh}	.11
	Carnation Creek, Vancouver Island, Canada	0.11	0.05	+0.06	315	Ab, Ts, Th	M_{gr} M_{sr} M_c	.45
	Cedar River, WA, U.S.	o	0.02	+?	136	Ps	S_s	
	Clear Lake, Ontario, Canada (25)	0.35	0.09	+0.26	90	Ac, F, Q	I_{gr} M_g	.26
	ELA, Ontario, Canada	0.32	0.05	+0.27	83	Pin, Pic	I_{gr} M_g	.16
	Finland	0.1	0.3	-0.2	57	Pin, Pic, B	I_{gr} M_g	3.00
	Storsjon, Sweden	0.14	0.02	+0.12	87	Pin, Pic	I_g	.14
	Western Cascades Range, OR, U.S	0.29[p]	0.51[p]	-0.22	200	Ps	I_b	1.76 Avg. .85
Temperate: bog vegetation	Rough Sike Catchment, England	0.6	0.4[f]	+0.2	213	Bog	S_{cr} S_{si} S_{sh}	.67
Tropical: angiosperm, mostly evergreen forest	Rio Negro, Brazil	0.2	0.1[g]	+0.1	213	Trp	S_{shr} M_{shr} M_g	.50
Tundra: low shrub vegetation	Kuokkel area, Sweden	0.055[m]	0.041[m]	+0.014	75	Ca, Em, B	M_{sh}	.75 Grand Avg. = 0.78
			Nitrogen					
Temperate: mostly angiosperm and deciduous forest	Coshocton, OH, U.S. (21)	20	2.5	+17.5	89	L, Pin	S_{shr} S_{cr} S_s	.125
	Hubbard Brook, U.S.	20.7[i,j]	4.0[i]	+16.7	130	Ac, F, B	I_{gr} M_{sh}	.19
	S.E. U.S.	2[k]	1[k]	+1[k]	127	Q, Pin	S_{sr} S_{shr} M_{sh}	.50
	Silverstream, New Zealand	2.2	1.8	+0.4	135	N	S_{sr} S_{shr} M_{gr} M_{sh}	.82
	Taughannock Creek, NY, U.S.	9.7[i]	5.6[i]	+4.1	95	Ac, Ti, Ts	S_{shr} S_c	.58
	Walker Branch, TE, U.S.	8.7	1.8	+6.9	155	Q, C	S_c	.21 Avg. = .40
Temperate: mostly coniferous and evergreen forest	Birkenes Watershed, Norway	14.5[i]	2.2[i]	+12.3	134	B, Pin, Pic	I_g	.15
	Carnation Creek, Vancouver Island, Canada	2.7[i]	1.1[i]	+1.6	315	Ab, Ts, Th	M_{gr} M_{sr} M_c	.41
	Cedar River, WA, U.S.	1.1	0.6[d]	+0.5	136	Ps	S_s	.54
	ELA, Ontario, Canada	6.4	0.9	+5.5	83	Pin, Pic	I_{gr} M_g	.14
	Finland	6	2	+4	57	Pin, Pic, B	I_{gr} M_g	.33
	Storsjon, Sweden	10.0	2.3	+7.7	67	Pin, Pic	I_{gr}	.23
	Velen, Sweden	5.9[e,i]	0.4[e,i]	+5.5	72	Pin, Pic	M_g I_g	.07
	Western Cascades Range, OR, U.S. (22)	2.5[i]	1.2[i]	+1.3	200	Ps	I_b	.55 Avg. = .30
Temperate: bog vegetation	Rough Sike Catchment, England	8.2	3.0[f]	+5.2	213	bog	S_{cr} S_{si} S_{sh}	.36
Tropical: angiosperm mostly evergreen forest	Rio Negro, Brazil	5.6	4.7[g]	+0.9	230	Trp	S_{shr} M_{shr} M_g	.84
Tundra: low shrub vegetation	Kuokkel area, Sweden (23)	1.15[m]	0.97[m]	+0.18	75	Ca, Em, B	M_{sh}	.84 Grand Avg. = .40

Source: Likens, *et al.* (1977)

[b] Vegetation footnotes: Ab, Abies, Ac, Acer, B, Betula, Bog, bog species; C. Carya; Ca, Calluna; E. Eucalptus; Em, Empetrum; F, Fagus, J, Juniperus; L, locust, N, Nothofagus, Pin, Pinus; Pic, Picea; Ps. Pseudotsuga; Po. Populus; Q, Quercus; Th, Thuja; Ti, Tilia; Ts, Tsuga, Trp, tropical species.

[c] Geology footnotes, I_{gr}, igneous, granitic; I_b, igneous, basaltic; S_c sedimentary, carbonate; S_{shr}, sedimentary, shale; S_{si}, sedimentary, sandstone, M_x, metamorphic (x refers to subscripts used above).

[d] To water table.

[e] Average for 6 yr, 1968-1973.

[f] Transport of eroded peat not included.

[g] Assuming measurements of discharge and concentration are representative of the entire year.

[h] Calculated from Mg inputs and Na Mg ratio in seawater.

[i] NO_3-N +NH_4-N.

[j] Average of five drainage basins, 1971-1973.

[m] Average for 5 yr. 1971-1975.

[n] Calculated from 89 cm of precipitation times concentration (0.02 mg P/l; Taylor *et al.*, 1971).

[o] "Trace."

[p] Average of five drainage basins, 1972-1973.

[q] Data for calcium omitted because of apparent contamination of precipitation samples.

TABLE III-19

SALT YIELDS FROM IRRIGATION IN GREEN RIVER SUBBASIN (EPA, 1971)

Area	Average salt yield		
	(tons/acre/yr)	(kg/ha/day)	(lb/acre/day)
Green River above New Fork River	0.1	0.6	0.5
Big Sandy Creek	5.6	34.3	30.7
Blacks Fork in Lyman area	2.4	14.7	13.2
Hams Fork	0.3	1.8	1.6
Henry's Fork	4.9	30.1	26.9
Yampa River above Steamboat Springs	0.2	1.2	1.1
Yampa River, Steamboat Springs to Craig	0.4	2.5	2.2
Mill Creek	0.1	6.1	5.4
Williams Fork River	0.3	1.8	1.6
Little Sanke above Dixon	0.3	1.8	1.6
Little Sanke, Dixon to Baggs	0.5	3.1	2.7
Ashley Creek	4.2	25.8	23.0
Duchesne River	3.0	18.4	16.4
White River below Meeker	2.0	12.3	11.0
Price River	8.5	52.2	46.6
San Rafael River	2.9	17.8	15.9

TABLE III-20

SALT YIELDS FROM IRRIGATION IN UPPER COLORADO MAIN STREAM SUBBASIN (EPA, 1971)

Area	Average salt yield		
	(tons/acre/yr)	(kg/ha/day)	(lb/acre/day)
Main stem above Hot Sulphur Springs	0.3	1.8	1.6
Main stem, Hot Sulphur Springs to Kremmling	0.9	5.5	4.9
Muddy Creek Drainage Area	2.4	14.7	13.2
Brush Creek	0.7	4.3	3.8
Roaring Fork River	3.5	21.5	19.2
Colorado River Valley, Glenwood Springs to Silt	2.3	14.1	12.6
Colorado River, Silt to Cameo	3.5	21.5	19.2
Grand Valley	8.0	49.1	43.8
Plateau Creek	0.9	5.5	4.9
Gunnison River above Gunnison	0.3	1.8	1.6
Tomichi Creek above Parlin	0.3	1.8	1.6
Tomichi Creek, Parlin to mouth	0.3	1.8	1.6
Uncompahgre above Dallas Creek	4.5	27.6	24.7
Lower Gunnison	6.7	41.1	36.7
Naturita Creek near Norwood	2.8	17.2	15.3

TABLE III-21

SALT YIELDS FROM IRRIGATION IN SAN JUAN RIVER SUBBASIN (EPA, 1971)

	Average salt yield		
	(tons/acre/yr)	(kg/ha/day)	(lb/acre/day)
Fremont River above Torrey, Utah	0.4	2.5	2.2
Fremont River, Torrey to Hanksville, Utah	5.8	35.6	31.8
Muddy Creek above Hanksville, Utah	3.1	19.0	17.0
San Juan above Carracas	2.7	16.6	14.8
Florida, Los Pinos, Animas drainage	0.2	1.2	1.1
Lower Animas Basin	3.5	21.5	19.2
LaPlata River in Colorado	1.4	8.6	7.7
LaPlate River in New Mexico	0.3	1.8	1.6

TABLE III-22

SALT YIELDS FROM IRRIGATION IN LOWER COLORADO RIVER BASIN (EPA, 1971)

Area	Average salt yield (tons/acre/yr)	(kg/ha/day)	(lb/acre/day)
Virginia River	2.3	14.1	12.6
Colorado River Indian Reservation	0.5	3.1	2.7
Palo Verde Irrigation District	2.1	12.9	11.5
Below Imperial Dam (Gila and Yuma projects)	variable	-	-

TABLE III-23

SALT YIELDS FROM IRRIGATION FOR SELECTED AREAS IN CALIFORNIA
(WATER RESOURCES COUNCIL, 1971)

Area	Average salt yield (tons/acre/yr)	(kg/ha/day)	(lb/acre/day)
North coastal	0.353	2.2	1.9
Central coastal	0.808	5.0	4.4
Sacramento	0.707	4.3	3.9
Delta-Central Sierra	0.974	6.0	5.3
San Joaquin	0.827	5.1	4.5
Tulare	0.768	4.7	4.2
Colorado Desert	10.9	67	60

values are site specific. An average salt pickup rate might be 5 MT/ha/year (2 tons/acre/year). On a per day basis, the range becomes 3 to 50 kg/ha/day (3 to 44 lb/acre/day), and the average becomes 12 kg/ha/day (11 lb/acre/day).

The most common means of expressing the salinity of water is its electrical conductivity. Conductivity is the inverse of resistance (ohms) and is expressed in units of "mhos".

The salt pick up in an irrigation water as it is diverted from a river through a field and returns to the river can be measured by the change in the conductivity of the water. The conductivity of the drainage water can be determined from the conductivity of the irrigation water and the leaching fraction (USDA, 1954) by

$$EC_{dw} = ECi_{w}/(LF) \tag{III-22}$$

where EC_{dw} = drainage water conductivity (umho)
EC_{iw} = irrigation water conductivity (umho) and
LF = leaching fraction

The usual range of the leaching fraction is about 0.1 to 0.3.

The conductivity of the irrigation water is related almost linearly to the concentration of the salt. Thus the concentration of salt can be determined from the conductivity and vice versa. The general model is

$$S = aK \tag{III-23}$$

where

S is the dissolved solids concentration (mg/l)
K is the conductance (umho) and
a is a regression coefficient

The value of a is usually between 0.55 and 0.75 with higher values generally occurring in waters having higher sulfate concentrations (Hem, 1970). An average value is about 0.63.

Another important parameter affecting the quality of water for irrigation is the sodium adsorption ratio (SAR). This is defined as

$$SAR = \frac{[Na]}{\sqrt{\frac{[Ca + Mg]}{2}}} \tag{III-24}$$

where

SAR is the sodium adsorption ratio (meq/l)

[Ca+Mg] is the concentration of calcium plus magnesium in the irrigation water (meq/l) and

[Na] is the concentration of sodium in the irrigation water (meq/l)

The SAR is a measure of the sodium hazard of irrigation water to plants. Like the EC, the SAR of irrigation drainage water can be calculated knowing the SAR of the irrigation water and the leaching fraction (Bower, et al., 1968) by

$$SAR_{dw} = \frac{SAR_{iw}}{\sqrt{LF}} \tag{III-25}$$

where

dw denotes drainage water and
iw denotes irrigation water.

This equation assumes that no precipitation or dissolution of salts occurs in the soil during irrigation.

3.2.9 Toxic Chemicals in Agricultural Environment

The primary group of toxic chemicals that will be of concern in agricultural or forested settings will be the pesticides including herbicides, insecticides, etc. Metals and other organic materials may be a problem if municipal sludges or landfills are of concern. These problems will not be dealt with in this text however. In addition the discussion will be limited to those insecticides occurring on the EPA 129 priority pollutant list.

While pesticides may be lost during application, enter the air and be diffusely redeposited and washed off the land surface, this mechanism will not be as great a pathway for loss as washoff from the field surface to which the pesticide is applied. It will be assumed that the only sources of pesticides will be slug applications to the surface in a short time period following which the pesticide will disappear at some first order rate. It is important that the amount of pesticide remaining on the watershed surface be known at the time of the storm event. Another important quantity to know is the amount of pesticide that is adsorbed onto soil materials versus that quantity which is dissolved in the soil solution. This ratio greatly affects the amount of pesticide lost in the runoff. Thus for toxic pollutants three key processes must be described in order to simulate their magnitude in runoff losses:

- the rate at which they accumulate or are deposited at the watershed surface

- the rate at which they disappear from the watershed surface and

- the ratio with which they partition themselves between the dissolved and sorbed phases.

3.2.9.1 Disappearance of Pesticides from the Watershed Surface

Pesticides are lost from the watershed surface after application through several important processes:

1. leaching
2. runoff
3. volatilization
4. degradation and
5. plant uptake

Pesticides which have low water solubilities and are strongly adsorbed to soil materials are most resistant to leaching. Chlorinated hydrocarbons (e.g. aldrin, chlordane, DDT, endrin, dieldrin, endosulfan, heptachlor, toxaphene) fall into these categories. They tend to be adsorbed hydrophobically and to a greater extent in soils with high organic carbon contents. Nonbiological degradation is thought to be a minor mode of loss for chlorinated hydrocarbons (El Beit, *et al.*, 1981) as well as chemical degradation. They are degraded biologically however, especially under anaerobic conditions (Kaufman, 1974).

Volatilization is apparently one of the major pathways of loss of organochlorine pesticides from the soil. Many factors affect volatilization rates including sorption, concentration, soil water/air flow rate, temperature, diffusion and physical and chemical properties of the pesticides.

The two factors that most affect plant uptake are polarity and water solubility (Nash, 1974). Although polar, the chlorinated hydrocarbons are relatively insoluble in water and plant uptake is probably not a great mechanism of loss.

Usually runoff losses are greatest for those pesticides with long half lives and those which are strongly adsorbed to soil materials. These pesticides tend to remain on the surface for long periods of time where they continue to be lost in eroded sediments.

Except for the processes of leaching and runoff losses which will be described mathematically, this methodology for calculating pesticide runoff losses will assume that the disappearance of pesticide from the soil surface is first order. The rate constant k_s, for this disappearance is the sum of the rate constants for all the individual processes of volatilization, degradation, etc.

The equation which gives the quantity of pesticide in the soil surface layer (1 cm) is (Haith, 1980):

$$P_t = P_\tau^* \exp\left[-k_s\,(t-\tau)\right] \qquad \text{(III-26)}$$

where

P_t is the pesticide remaining on day t

P_τ^* is the amount of pesticide in the soil on the day of the last rainfall event or pesticide application event

k_s is the disappearance rate constant

t is the number of the day of the runoff event and

τ is the number of the day of the last runoff event or application event.

If the event on day t was a rainfall event then

$$P_\tau^* = P_\tau - PX_\tau - (1-\theta/R_\tau)D_\tau \qquad \text{(III-27)}$$

or if the event was a pesticide application

$$P_\tau^* = P_\tau + \Delta P_\tau \qquad \text{(III-28)}$$

The parameters PX_τ, θ, R_τ and D_τ are discussed in section 3.2.9.3. Degradation rate coefficients (k_s) can be estimated for most of the chlorinated hydrocarbons on the priority pollutant list by choosing a representative value from either Table III-24 or Table III-25.

3.2.9.2 Partitioning of Pesticides between Soil and Water

Sorption refers to the removal of pesticide from solution by soil materials. Adsorption mechanisms on clay minerals include cationic and anionic exchange, hydrogen bonding and Van der Waals attraction. Adsorption onto organic matter is a result of cation or anion exchange, hydrogen bonding, and/or hydrophobic bonding.

TABLE III-24

VALUES OF k_s FOR DISSIPATION OF PESTICIDES FROM SOIL SURFACES

Pesticide	Soil			Crop or conditions	Application rate	k_s
	Type	pH	OM			
			(%)		(kg/ha)	
Aldrin	Coachella fs				20.2	0.2406
Aldrin (+dieldrin) (granules)	Carrington sil				5.6	.0045
Aldrin						< .0032
Aldrin	Ulysses sil			Fallow	2.24	.0264
Aldrin	Knox sil			Fallow	2.24	.0259
Aldrin	Celeryville muck			Fallow	2.24	.0014
Aldrin	Marietta sl			Fallow	2.24	.0136
Aldrin	Fox fsl			Fallow	2.24	.0256
Aldrin	Miami sil			Fallow	2.24	.0258
Aldrin	Muck			Fallow	2.24	.0066
Aldrin	Carrington sil	Nondisked		Fallow	4.5	.0101
Aldrin	Carrington sil	Disked		Fallow	4.5	.0136
Aldrin	Udaipur cl	7.8	1.6	Various	3.0	.0149 $\bar{x}$ of 19 $\bar{x}$ of 19
Aldrin	Jobner	8.6	.26	Various	3.0	.0165 $\bar{x}$ of 19
Aldrin	Muck				22.4	.0061
Aldrin	Miami sil				22.4	.0096
Aldrin	Composite				22.4	.0038
Aldrin (Dieldrin)	Carrington sil	Nondisked			4.5	.0006
Aldrin (Dieldrin)	Carrington sil	Disked			4.5	.0008
Aldrin (Dieldrin)	Carrington sil	Disked		Granules	5.6	.0012

(continued)

TABLE III-24 (continued)

Pesticide	Soil			Crop or conditions	Application rate	k_s
	Type	pH	OM			
			(%)		(kg/ha)	
Aldrin (Dieldrin)	Carrington sil			Spray		.0017
BHC						.0021
BHC	Udaipur	7.8	1.6	Various	5.0	.0140
BHC						$\bar{x}$ of 19
BHC	Jobner sl	8.6	.26	Various	5.0	.0098 $\bar{x}$ of 19
BHC alpha	Berwick sl			Vegetables	7.4 BHC	.0006
BHC beta	Berwick sl			Vegetables	7.4 BHC	.00015
BHC gamma	Berwick sl			Vegetables	7.4 BHC	.00042
BHC delta	Berwick sl			Vegetables	7.4 BHC	.00036
Chlordane	Berwick sl				2.0	.00072
Chlordane	Composite					.0020
Chlordane	Gullatin Valley			Alfalfa	2.0	.0101
Chlordane	Gullatin Valley			Alfalfa	>2	.007
DDT	sl				83	.004
DDT	Coachella fs				22.4	.053
DDT	Houston c	>7				.0060
DDT	Pima sic	>7				.0049
DDT	Pinal gl	>7				.0060
DDT	Blackwater River	<7		Forest	1.12	.00015
DDT	Pollard Mountain	<7		Forest	1.12	.000023
DDT	Mosquito Bnk Pod	<7		Forest	1.12	.00040
DDT	Route 11	<7		Forest	1.12	.00014
DDT	West Oxbow	<7		Forest	1.12	.00024
DDT	Beach Mountain	<7		Forest	1.12	.00044
p,p'-DDT	Carrington sil	Nondisked			4.5	.0024
p,p'-DDT	Carrington sil	Disked		Fallow	4.5	.0048
p,p'-DDT	Miami sil				11.6	.0003

(continued)

TABLE III-24 (continued)

Pesticide	Soil			Crop or conditions	Application rate	k_s
	Type	pH	OM			
			(%)		(kg/ha)	
p,p'-DDT	Carrington sil	Disked/non-disked		Fallow	4.5	.0002
p,p'-DDT	Muck				11.2	.0011
p,p'-DDT	Miami sil				11.2	.0029
p,p'-DDT	Berwick sl				37 DDT	.00016
p,p'-DDT	Composite					.0007
o,p'-DDT	Berwick sl					.00029
p,p'-DDT	Ulysses sil	6.9	1.8	Fallow	9.4	.0008
p,p'-DDT	Knox sil	6.8	.8	Fallow	9.4	.0005
p,p'-DDT	Celeryville muck	4.9	74.5	Fallow	9.4	.0021
p,p'-DDT	Marietta sl	6.0	2.0	Fallow	9.4	.0014
p,p'-DDT	Fox fsl	7.2	.8	Fallow	9.4	.0009
p,p'-DDT	Miami sil	7.1	3.6	Fallow	9.4	.0004
p,p'-DDT	Muck	6.8	40.0	Fallow	1.0	.0009
p,p'-DDT	Commerce sil				24.4	.0037
Dieldrin	Carrington sil	Nondisked		Fallow	4.5	.0142
Dieldrin	Carrington sil	Disked		Fallow	4.5	.0187
Dieldrin						.0003
Dieldrin	Imperial sc	7.8	1.0		20.0	.0002
Dieldrin	Holtville fsl	7.8	.5		20.0	.0001
Dieldrin	Composite					.0008
Endosulfan	Various				1.3	.0162
Endrin	Mhoon sicl	6.0	1.2	Sugarcane		.0110
Endrin	Coachella fs				5.4	.2436
Heptachlor	Composite					.0021
Heptachlor	Composite					.0025
Heptachlor	Composite					.0028
Lindane	Imperial sc	7.8	1.0		20	.0022
Lindane	Holtville fsl	7.8	.5		20	.0026
Lindane	Composite					.0017

(continued)

TABLE III-24 (continued)

Pesticide	Soil			Crop or conditions	Application rate	k_s
	Type	pH	OM			
			(%)		(kg/ha)	
Lindane	Gila sil	7.7	.6	None		2/.0046
Lindane	Miami sil				11.6	.0011
Lindane	Muck				11.2	.0014
Lindane	Miami sil				11.2	.0048
Lindane	Ulysses sil			Fallow	1.12	.0147
Lindane	Knox sil			None	11.2	.0264
Lindane	Celeryville muck			None	11.2	.0074
Lindane	Marietta sl			None	11.2	.0263
Lindane	Fox fsl			None	11.2	.0264
Lindane	Miami sil			None	11.2	.0139
Lindane	Muck			None	11.2	3/.0059
Toxaphene	Galestown sl	6.7	5.2	Cotton	(6x2.7)	.0046

1/ si = silt; s = sand; sh = shale; c = clay; l = loam; f = fine; g = gravelly.

Source: Nash, 1980.

TABLE III-25

DEGRADATION RATES COEFFICIENTS FOR SELECTED PESTICIDES

Pesticide	Conditions	k_s	%CV	Half Life
Aldrin	Lab	0.013		53
	Field	0.0023	100.	1237
Chlordane	Field	0.0024	104.2	1214
DDT	Lab	0.00013	130.8	1657
	Lab (anaerobic)	0.0035	82.7	692
Dieldrin	Lab	0.013		53
	Field	0.0023	100.	1237
Endrin	Lab (anaerobic)	0.03	53.3	31
	Field	0.0015		460
	Field (anaerobic)	0.0053		130
Heptachlor	Lab	0.011		63
	Field	0.0046	119.6	426
Lindane (γ-BHC)	Lab	0.0026		266
	Lab (anaerobic)	0.0046		151

Source: Rao and Davidson (1980)

Pesticides can be broken down into two categories

1. ionic and
2. nonionic

If pesticides are ionic they are in general cationic, basic or acidic. Their primary mechanism of sorption is through ion exchange when in their ionic form. Chlorinated hydrocarbons are nonionic and their major mechanism of sorption appears to be hydrophobic bonding. Therefore their sorption is highly related to the amount of organic carbon in the soil (Woodard and Weber, 1974).

For hydrophobic sorption the partition coefficient K_d can be most successfully estimated using the octanol-water partition coefficient and the following equations (Rao and Davidson, 1980):

$$\log K_{oc} = 1.03 \log K_{ow} - 0.18 \tag{III-29}$$

and

$$K_d = \frac{K_{oc} \cdot \%OC}{100} \tag{III-30}$$

where

K_{ow} is the octanol - water partition coefficient,

K_{oc} is the organic carbon partition coefficient

$\%OC$ is the percent soil organic carbon and

K_d is the adsorption partition coefficient (cm^3/g)

Values of K_{ow}, K_{oc} and K_d are given in Table III-26 for some of the chlorinated hydrocarbons on the priority pollutant list.

TABLE III-26

OCTANOL-WATER PARTITION COEFFICIENTS FOR SELECTED PESTICIDES[1]

Pesticide	Kow	Koc	Kd
Aldrin			2.8
Chlordane	2.1E3		
DDD	1.2E5		
DDE	7.3E4		
DDE$_{p,p}$	4.9E5		
DDT	3.7E5	2.4E5	4.2E4
DDT$_{p,p}$	1.5E6		
Dieldrin	4.9E3		6.3E2
Endrin	1.6E3		
Heptachlor	7.4E3		
Lindane (γ-BHC)	6.4E2	1.1E3	20.1
Toxaphene	1.7E3		

[1] Kow and Koc from Rao and Davidson, 1980.
Kd from Pionke and DeAngelis, 1980.
Kd Lindane from Rao and Davidson, 1980.

3.2.9.3 Determination of Pesticide Runoff Loss

To determine the magnitude of runoff loss the quantity of adsorbed and dissolved pesticide is first determined. Total pesticide is the sum of the adsorbed and dissolved fractions

$$P_t = A_t + D_t \qquad \text{(III-31)}$$

The adsorbed quantity A_t is given by

$$A_t = [1/(1 + \theta/K_d\rho)]\ P_t \qquad \text{(III-32)}$$

while the dissolved fraction, D_t, is

$$D_t = [1/(1 + {}^{K_d\rho}/\theta)]\ P_t \qquad \text{(III-33)}$$

The loss of adsorbed pesticide is

$$PX_t = [Y(S)_E/100\rho]\ A_t \qquad \text{(III-34)}$$

and the dissolved pesticide loss is

$$PQ_t = [Q/R_t]\ D_t \qquad \text{(III-35)}$$

In the above equations

A_t = sorbed pesticide loss (Kg/ha, lb/ac)

θ = available water capacity of the top cm of soil (difference between wilting point and field capacity) (dimensionless)

ρ = soil bulk density (g/cm^3)

P_t = total pesticide concentration (kg/ha, lb/acre)

D_t = dissolved pesticide concentration (kg/ha, lb/acre)

PX_t = sorbed pesticide loss (kg/ha, lb/acre)

PQ_t = dissolved pesticide loss (kg/ha, lb/acre)

Q = total storm runoff depth (in, cm)

R_t = total storm rainfall depth (in, cm) and

K_d = sorption partition coefficient (cm^3/g)

An example problem for determining the runoff losses of a chlorinated hydrocarbon follows.

EXAMPLE III-4

Estimation of Lindane Loss From an Agricultural Watershed

On 5 June an application of 5.0 kg/ha of lindane (γ-BHC) was made to the corn crop on the watershed in Example III-1. There was lindane residue of 1.0 Kg/ha already in the soil. On June 8 the rainfall event evaluated in Example III-2 occurred. Runoff from this storm was 0.20 cm and the total sediment loss was 45.5 metric tons. The soil is a Fayette Silt Loam (sil) with $\theta = 0.3$ and 10 percent organic carbon. The bulk density is 1.2 g/cm³. Evaluate the lindane loss in sediment and water.

Solution:

First the amount of lindane in the surface layer on 8 June, three days after application, must be estimated. Using Equation III-28

$$P_t^* = 1.0 + 5.0 = 6.0 \text{ kg/ha}$$

of lindane on June 5. Looking over the k_s values for lindane in silty loam soils, values of .0011 to .0164 per day are found. To simulate worst case, the smallest disappearance rate will be used.

From Equation III-26

$$\begin{aligned} P_t &= 6.0 \exp[-0.0011(3)] \\ &= 5.98 \text{ Kg/ha} \end{aligned}$$

The dissolved and adsorbed fractions of lindane must be known. The K_{ow} according to Rao and Davidson (Table III-26) is 643. Using Equation III-29

$$\begin{aligned} \log K_{oc} &= 1.03 [\log (643.)] - 0.18 \\ &= 2.71 \\ K_{oc} &= 516. \end{aligned}$$

Using 10 percent soil organic carbon and Equation III-30,

$$K_d = \frac{516(10)}{100} = 51.6 \frac{\text{cm}^3}{\text{g}}$$

The dissolved and adsorbed portions are

$$\begin{aligned} D_t &= [1/(1 + (51.6 \cdot 1.2)/.3)]\ 5.98 \\ &= 0.03 \text{ kg/ha} \end{aligned}$$

$$\begin{aligned} A_t &= [1/(1 + .3/(51.6 \cdot 1.2))]\ 5.98 \\ &= 5.95 \text{ Kg/ha} \end{aligned}$$

The lindane lost due to erosion is (Equation III-34)

$$\begin{aligned} PX_t &= [45.5/(72.8 \cdot 100 \cdot 1.2)]5.95 \\ &= 0.03 \text{ kg/ha} \end{aligned}$$

The lindane lost due to runoff is (Equation III-35)

$$\begin{aligned} PQ_t &= [0.2/4.5]\ 0.03 \\ &= .001 \text{ kg/ha} \end{aligned}$$

The total loss of lindane is the sum of PQ_t and PX_t times the total area or

$$\begin{aligned} P_{total} &= (0.03 + 0.001)(72.8) \\ &= 2.26 \text{ kg} \end{aligned}$$

It is evident that lindane travels primarily with sediment and that erosion control practices would be effective in reducing lindane losses. This will not be the case for all pesticides but will be true for most chlorinated hydrocarbons.

END OF EXAMPLE III-4

3.3 URBAN NONPOINT SOURCE LOADS

From established urban areas, stormwater may pick up various wastes ranging from settled dust and ash to debris coming directly from man himself. The quantities of solids from urban nonpoint sources are quite significant in quantity. Fly ash and dust from industrial processes such as steel mills, cement manufacturing, and certain chemical processes are known to be profuse. Dusts from the burning of organic fuels are a significant factor, and solids in sizable quantities also result from off-street mud, automotive exhaust, organic debris from tree leaves and grass trimmings, and discarded litter.

In this report, the nonpoint source loading calculation for conventional pollutants follows the procedures contained in a recent EPA study (Heaney, et al., 1976). This procedure is used for annual loadings. For storm event loadings, excerpts from another EPA study (Amy, et al., 1974) are utilized. The original procedure has been modified to make it more realistic in terms of pollutant accumulation.

3.3.1 Annual Urban Loads

The predictive equation in this procedure allows the user to make a determination of average annual loads of BOD_5, suspended solids, volatile solids, PO_4 and Total N as a function of land use, type of sewer system, precipitation, population density and street sweeping frequency. The procedure requires little external data. The loading equation is

$$\overline{M}_j = a \cdot P \cdot \sum_{i=1}^{4} \varepsilon_i \cdot (\alpha_{ij}) \cdot f_{2_i}(PD_d) \cdot \gamma \qquad \text{(III-36)}$$

In this equation

P = annual precipitation (in) (cm)

ε_i = fraction of urban area that is made up of the following land uses:

1) Residential
2) Commercial
3) Industrial
4) Other developed (parks, cemeteries, schools, etc.)

α_{ij} = pollutant loading factor (lb/acre-in, kg/ha-cm) for land use 'i'.

$f_{2_i}(PD_d)$ = population density functions for land use 'i' and

γ = the street sweeping frequency

a = a units conversion
1.0 English units
0.442 metric units and

$\overline{M}_j$ = the annual area weighted load of pollutant 'j' (lb/acre-yr, kg/ha-yr)

Evaluation of Factors in the Loading Function

The value of ε_i is determined from areal photographs or may come from talking to local sources such as city planners or engineers. When better data are lacking, Table III-27 may provide some general guidance.

Values for α_{ij} are found in Table III-28. Notice that a different set of α_{ij} are used for separate and combined sewer systems.

The population density function is given by the following set of equations

Residential (i = 1)

$$f_2(PD_d) = 0.142 + 0.218\ (PD_d)^{0.54} \qquad \text{(III-37)}$$

Commercial - Industrial (i = 2,3)

$$f_2(PD_d) = 1.0 \qquad \text{(III-38)}$$

Other developed (i = 4)

$$f_2(PD_d) = 0.142 \qquad \text{(III-39)}$$

The population density PD_d must be obtained locally.

The street sweeping factor γ is evaluated by the following equations

$$\gamma = N_s/20 \qquad (0 \leq N_s \leq 20 \text{ days}) \qquad \text{(III-40)}$$

$$\gamma = 1.0 \qquad (N_s > 20 \text{ days}) \qquad \text{(III-41)}$$

Where

N_s is the street sweeping interval (days)

TABLE III-27

GENERAL LAND CONSUMPTION RATES FOR VARIOUS LAND USES (AMERICAN PUBLIC WORKS ASSOCIATION, 1974)

Land Use	Land consumption (acres/capita) <100,000 Population	 >100,000 Population	 >250,000 Population
Residential	0.1049	0.0714	0.0585
Commercial	0.0101	0.0084	0.0073
Industrial	0.0177	0.0083	0.0077
Park	0.0146	0.0093	0.0078

TABLE III-28

POLLUTANT LOADING FACTORS ($\alpha_{i,j}$)

	Land Use, i	1. BOD_5	2. SS	3. VS	4. PO_4	5. N
Separate Areas,	1. Residential	0.799	16.3	9.45	0.0336	0.131
	2. Commercial	3.20	22.2	14.0	0.0757	0.296
	3. Industrial	1.21	29.1	14.3	0.0705	0.277
	4. Other	0.113	2.70	2.6	0.00994	0.0605
Combined Areas,	1. Residential	3.29	67.2	38.9	0.139	0.540
	2. Commercial	13.2	91.8	57.9	0.312	1.22
	3. Industrial	5.00	120.0	59.2	0.291	1.14
	4. Other	0.467	11.1	10.8	0.0411	0.150

It is evident from Table III-20 that higher loads for all pollutants will be generated if combined sewers are specified. The data of Lager and Smith (1974) (Tables III-29, 30) suggest that the ratio of 4.12 for loads from combined areas to separate areas is good for BOD_5, N, and P (assumed in the above methodology). Suspended solids loads on the average appear to be less from combined areas than separate areas. Total coliform loadings on the other hand appear to be over an order of magnitude greater from combined than from separately sewered areas. The above trends are also verified by the data in Tables III-29, 30, 31 with the exception of total N.

EXAMPLE III-5

Estimation of Annual Urban Pollutant Loads

Consider a city of 10,000 acres of which 20 percent is commercial, 10 percent industrial, 65 percent residential and 5 percent is in other developed areas. The residential population density is 10 persons/acre. Most of the city has separate sewers but approximately 30 percent of the residential area still has combined sewers. The streets are swept every five days in the commercial and industrial areas and are not swept in the residential areas. The mean annual precipitation is 42 inches. Determine the average annual loadings of total nitrogen and phosphate.

Solution:

The population density function value for the residential area is (Equation III-37)

$$f_2\ (PO_d) = 0.142 + 0.218(10)^{0.54}$$
$$= .90$$

The street sweeping parameter is (Equation III-40)

$$\gamma = 5/20 = .25$$

TABLE III-29

COMPARISON OF QUALITY OF STORM SEWER DISCHARGES FOR VARIOUS CITIES[a] (LAGER AND SMITH, 1974)

Type of wastewater, location, year, Ref. No.	BOD_5, mg/l		COD, mg/l		DO, mg/l	SS, mg/l		Total coliforms, MPN/100 ml		Total nitrogen, mg/l as N	Total phosphorus, mg/l as P
	Avg	Range	Avg	Range	Avg	Avg	Range	Avg	Range	Avg	Avg
Typical untreated municipal	200	100-300	500	250-750	--	200	100-350	$5x10^7$	$1x10^7-1x10^9$	40	10
Typical treated municipal											
Primary effluent	135	70-200	330	165-500	--	80	40-120	$2x10^7$	$5x10^6-5x10^{[illegible]}$	35	7.5
Secondary effluent	25	15-45	55	25-80	--	15	10-30	$1x10^3$	$1x10^2-1x10^4$	30	5.0
Storm sewer discharges											
Ann Arbor, Mich., 1965 (2)	28	11-62	--	--	--	2,080	650-11,900	--	--	3.5	1.7
Castro Valley, Calif., 1971-72 (14)	14	4-37	--	--	8.4	--	--	$2x10^4$	$4x10^3-6x10^4$	1.9[b]	--
Des Moines, Iowa, 1969 (6)	36	12-100	--	--	--	505	95-1,053	--	--	2.2	0.87
Durham, N.C., 1968 (1)	31	2-232	224	40-660	--	--	--	$3x10^5$	$3x10^3-2x10^6$[c]	--	0.18
Los Angeles, Calif., 1967-68 (19)	9.4	--	--	--	6.9	1,013	--	--	$3x10^3-2x10^6$	--	--
Madison, Wis., 1970-71 (17)	--	--	--	--	--	81	10-1,000	--	--	4.8	1.1
New Orleans, La., 1967-69[d] (16)	12	--	--	--	4.5	26	--	$1x10^6$	$7x10^3-7x10^8$	--	--
Roanoke, Va., 1969 (12)	7	--	--	--	--	30	--	--	--	--	--
Sacramento, Calif., 1968-69 (37)	106	24-283	58	21-176	--	71	3-211	$8x10^5$	$2x10^4-1x10^7$[c]	--	--
Tulsa, Okla., 1968-69 (33)	11	1-39	85	12-405	--	247	84-2,052	$1x10^5$	$1x10^3-5x10^8$	0.3-1.5[e]	0.2-1.2[f]
Washington, D.C., 1969 (5)	19	3-90	335	29-1,514	--	1,697	130-11,280	$6x10^5$	$1x10^5-3x10^6$	2.1	0.4

a. Data presented here are for general comparisons only. Since different sampling methods, number of samples, and other procedures were used, the reader should consult the references before using the data for specific planning purposes.

b. Only ammonia plus nitrate.

c. Only fecal.

d. Median values from 1 sampling station.

e. Only organic (Kjeldahl) nitrogen.

f. Only soluble orthophosphate.

TABLE III-30

COMPARISON OF QUALITY OF COMBINED SEWERS FOR VARIOUS CITIES[a], (LAGER AND SMITH, 1974)

Type of wastewater, location, year, Ref. No.	BOD_5, mg/l		COD mg/l		DO, mg/l	SS mg/l		Total coliforms, MPN/100 ml		Total nitrogen, mg/l as N	Total phosphorus, mg/l as P
	Avg	Range	Avg	Range	Avg	Avg	Range	Avg	Range	Avg	Avg
Typical untreated municipal	200	100-300	500	250-750	--	200	100-350	$5x10^7$	$1x10^7$-$1x10^9$	40	10
Typical treated municipal											
Primary effluent	136	70-200	330	165-500	--	80	40-120	$2x10^6$	$5x10^6$-$5x10^8$	35	7.5
Secondary effluent	25	15-45	55	25-80	--	15	10-30	$1x10^3$	$1x10^2$-$1x10^4$	30	5.0
Selected combined											
Atlanta, Ga., 1969 (31)	100	48-540	--	--	8.5	--	--	$1x10^7$	--	--	1.2[b]
Berkeley, Calif. 1968-69 (34)[c]	60	18-300	200	20-600	--	100	40-150	--	--	--	--
Brooklyn, N.Y., 1972 (8)	180	86-428	--	--	--	1,051	132-8,759	--	--	--	1.2[b]
Bucyrus, Ohio 1968-69 (35)	120	11-560	400	13-920	--	470	20-2,440	$1x10^7$	$2x10^5$-$5x10^7$	13	3.5
Cincinnati, Ohio, 1970 (36)	200	80-380	250	190-410	--	1,100	500-1,800	--	--	--	--
Des Moines, Iowa, 1968-69 (6)	115	29-158	--	--	--	295	155-1,166	--	--	12.7	11.6
Detroit, Mich., 1965 (2)	153	74-685	115	--	--	274	120-804	--	--	16.3[d]	4.3
Kenosha, Wis., 1970 (18)	129	--	464	--	--	458	--	$2x10^6$	--	10.4[d]	5.9
Milwaukee, Wis., 1969 (7)	55	26-182	177	118-765	--	244	113-848	--	$2x10^5$-$3x10^7$	3-24	0.8[b]
Northampton, U.K., 1960-62 (22)	150	80-350	--	--	--	400	200-800	--	--	10[c]	--
Racine, Wis., 1971 (18)	119	--	--	--	--	439	--	--	--	--	--
Roanoke, Va., 1969 (12)	115	--	--	--	--	78	--	$7x10^7$	--	--	--
Sacramento, Calif., 1968-69 (37)	165	70-328	238	59-513	--	125	56-502	$5x10^6$	$7x10^5$-$9x10^7$[9]	--	--
San Francisco, Calif., 1969-70 (3)	49	1.5-202	155	17-626	--	68	4-426	$3x10^6$	$2x10^4$-$2x10^7$	--	--
Washington, D.C., 1969 (5)	71	10-470	362	80-1,760	--	622	35-2,000	$3x10^6$	$4x10^5$-$6x10^6$	3.5	1.0

---

a. Data presented here are for general comparisons only. Since different sampling methods, number of samples, and other procedures were used, the reader should consult the references before using the data for specific planning purposes.

b. Only orthophosphate.

c. Infiltrated sanitary sewer overflow.

d. Only ammonia plus organic nitrogen (total) Kjeldahl).

e. Only ammonia.

f. Only fecal.

TABLE III-31

SUMMARY OF STORMWATER POLLUTANT CONCENTRATIONS (KAISER ENGINEERS, 1969)

	Stormwater Overflow Concentrations			
	Separate Drainage Areas[a]		Combined Areas[b]	
Pollutant[c]	Mean	Standard Deviation	Mean	Standard Deviation
BOD_5	27	25	108	36
COD	205	118	284	110
S.S.	608	616	372	275
Total Coliforms[d]	3×10^5	-	6×10^6	-
Total Nitrogen (as N)	2.3	1.4	9	6
Total Phosphorus (as P)	0.5	0.4	2.8	2.9

(a) Summary of 20 cities, storm sewers and unsewered areas

(b) Summary of 25 cities, combined sewer areas

(c) All units mg/l except coliforms, MPN/100 ml

(d) Geometric mean

Using Equation III-36,

$$\overline{M}_{\text{Ntotal}} = 42 \Bigg[\overset{\text{Residential}}{0.65\ (0.131 \cdot 0.70 + 0.54 \cdot 0.30)(.9)(1.0)}$$

$$\overset{\text{Commercial}}{+\ 0.20\ (0.296)(1.0)(0.25)}$$

$$\overset{\text{Industrial}}{+\ 0.10\ (0.277)(1.0)(0.25)}$$

$$\overset{\text{Other}}{+\ 0.05\ (0.060\text{S}9(0.142)(1.0)} \Bigg]$$

$$= 7.2\ \text{lb}\ \ /\text{acre-yr}$$

$$\overline{M}_{\text{PO}_4} = 42 \Bigg[\overset{\text{Residential}}{0.65\ (0.0336 \cdot 0.70 + 0.139 \cdot 0.30)(.9)(1.0)}$$

$$\overset{\text{Commercial}}{+\ 0.20\ (.0757)(1.0)(0.25)}$$

$$\overset{\text{Industrial}}{+\ 0.10\ (0.0705)(1.0)(0.25)}$$

$$\overset{\text{Other}}{+\ 0.05\ (0.0099)(0.142)(1.0)} \Bigg]$$

$$= \quad 1.8\ \text{lb-PO}_4/\text{acre-yr.}$$

Assuming the urban nonpoint source flow is untreated, the annual N and PO_4 loads to the stream are 36 tons - N/year and 9 tons-PO_4/year.

END OF EXAMPLE III-5

3.3.2 Estimation of Single Event Pollutant Loads

Two factors are of primary importance in determining pollutant loads from urban stormwater events. First, the accumulation (supply) of materials on the watershed must be accurately known and second, the capability of the system to move pollutants from the street surface to the stream must be estimated. The system here is a combination of rainfall event characteristics and watershed characteristics.

The accumulation of material on the watershed surface is addressed first.

3.3.2.1 Accumulation of Pollutants on Street Surfaces

The amount of material available to be washed off can be described as a function of the time since the latest of these events occurred. This time is called the equivalent days of accumulation (EDA) and is computed by

$$EDA = (D_R - D_S)\ (1 - \varepsilon_S) + D_S \qquad \text{(III-42)}$$

where

D_R = days since last "significant" storm event

D_S = days since last street sweeping event, and

ε_S = the street sweeping efficiency

According to Amy, et al., 1974, a "significant" storm event is one in which 0.5 inches falls within a period of one to five hours. A storm of this size is considered to remove 90 percent of the surface particulates.

Typical values for the street sweeping efficiency term, ε_S, are given in Table III-32. Notice that the efficiency is reduced for smaller particle sizes. Table III-33 shows the percent of solids, BOD_5, heavy metals and pesticides associated with different size fractions of debris, dirt and dust

TABLE III-32

SUMMARY OF STREET CLEANING METHODS

Type	Sweeping Action	Effectiveness			Travel Speed, mph	Sweeping Speed, mph	Total Cost	Special Limitations	Potential Problems			Special Advantages
		Debris Percent	Dirt Percent	Dust Percent					Parked Cars	Pavement Condition	Unimproved Streets	
Hand Cleaning	Pushbroom	95-100	Est. 70	Est. 45	Trucks Needed	Slow	High	Heavy Traffic	Minor	No	No	Adapt. to Special Needs
3 Wheel Mechanical	Gutter and Main Brooms	95-100	50-65	15-20	15-20	4-8	Medium	Wet, Snowy Streets	Major	Major	Not Useable	Maneuvers well
4 Wheel Mechanical	Gutter and Main Brooms	95-100	50-65	15-20	55	4-8	Medium	Wet, Snowy Streets	Major	Major	Not Useable	
Vacuum	Gutter Broom, Vacuum Pickup Head	95-100	60-80	40-70	55	4-10	Low	Less Maneuverability	Major	Minor	Not Effective	Wand can Clean Catch Basins
Air	Gutter Broom, Air Pump System	95-100	Est. 50-70	Est. 30-60	55	4-8	Low	Wet Streets	Major	Minor	Not Effective	
Flusher	Water Under Pressure	Small	30	Overall	55	12	Low	Very flat grades	No	No	Can't use if no drainage	

Source: Tetra Tech, Inc., 1978

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TABLE III-33

REMOVAL RATES FOR SELECTED CONTAMINANTS BY SIZE

Particle Size (μ)	Sweeper Efficiency (%)	Total Solids		BOD$_5$		Heavy Metals		Pesticides	
		Size Distr. (%)	Removal (%)	Size Distr. (%)	Removal (%)	Size Distri. (%)	Removal (%)	Size Distri. (%)	Removal (%)
>2,000	79	24.4	19.3	7.4	5.8	14.8	13.9	0	0
840-2,000	64	7.6	4.9	20.1	13.3	17.8	11.4	16	10.2
240-840	60	24.6	14.9	15.7	9.4	14.9	9.9	25.8	15.5
104-240	43	27.6	13.3	15.2	7.3	33.8	14.5	28.8	12.4
43-104	20	9.7	1.9	17.3	3.8	27.8	5.6	31.7	6.3
<43	15	3.9	0.9	24.3	3.4	- -	- -	- -	- -
Total Removal			55.2		43.0		55.3		44.4

Source: Sartor, J.D. and G.B. Boyd, 1972.

and their corresponding removal rates assuming the typical efficiencies in column 2 of the table.

Multiplication of EDA by the daily loading rate (lb day^{-1}) gives the total load of material on the street surfaces. (Residual loads remaining through pervious storm or sweeping events are not accounted for in this approach.) Notice that the removal of material will only be from street surfaces by this method. Material loads from previous areas in the watershed or nonconnected impervious areas will not be a calculated part of the load. Daily loading rates are calculated from the following procedure.

3.3.2.2 Street Surface Pollutant Loadings

Data developed in Amy, et al. (1974) include nationwide means of solids loading rates and pollutant composition of street solids, as well as a more detailed breakdown of data into major source categories. Table III-34 shows data from the URS report which are divided into 13 subsets among three major source categories including climate, land use, and average daily traffic. These data may be different from the means which are given in the last column of the table, at the 80 percent confidence level. Whenever the mean of any parameter (solid loading rates or composition) in any subset differs significantly from the mean of the set of all data, that number may be substituted for the mean of the set of all data. Table III-34 also gives the percent standard error of the mean which indicates the degree of confidence that may be placed on the mean.

3.3.2.2.1 Loading Functions for Solids

$$Y(S)_u = L(S)_u \cdot L_{st} \qquad \text{(III-43)}$$

where

$Y(S)_u$ = daily total solids loading, (kg/day, lb/day)
$L(S)_u$ = daily solids loading rates, (kg/curb-km-day, lb/curb-mile-day)

TABLE III-34

SOLID LOADING RATES AND COMPOSITION--NATIONWIDE MEANS AND SUBSTITUTIONS OF THE NATIONWIDE MEANS AT 80% CONFIDENCE LEVEL* (AMY, ET AL., 1974)

		lbs/curb mi/day	Concentrations in micrograms per gram of dry solid														No./gram	
	Category	Loading	BOD_5	COD	OPO_4	NO_3	OrgN	Cd	Cr	Cu	Fe	Pb	Mn	Ni	Sr	Zn	TCOLI+	FCOLI+
Climate	Northeast	291_c					$5,970_c$	2.6_b	139_b		$17,700_b$	870_c	363_a	21_c	27_b	260_b		$4.4E5_c$
	Southeast	103_b	$29,100_b$		$2,240_a$		$1,970_a$			137_b		$1,370_b$		21_b	28_b			$7.0E4_d$
	Southwest	50_c			470_b				241_a	78_a		$2,520_b$		57_b	15_a		$5.7E6_d$	
	Northwest	30_c							246_a		$34,500_b$	$2,600_b$			10_c	480_a	$6.8E5_f$	$1.1E4_f$
Land Use	Openspace																	
	Residential		$14,000_b$	$82,000_b$	850_b	550_c	$1,800_a$			93_a		$1,430_b$		28_b				
	Commercial	74_c	$58,700_c$	$269,000_c$	$2,250_c$	$1,580_c$	6.430_a			133_b		$3,440_b$		48_b		520_b		
	Light Industry																	
	Heavy Industry								278_b		$28,600_b$	$1,160_c$	570_b				$8.2E5_e$	
Average Daily Traffic No./day	< 500											$1,210_d$				252_b		$6.9E4_f$
	500-5,000		$9,500_c$	$83,000_c$	741_d	419_b					$18,900_a$	$1,060_c$		17_d	34_c			$3.4E5_d$
	5,000-15,000														18_a			
	< 15,000	82_d											357_a				$3.8E5_a$	
	All data**	156_b	$19,900_b$	$140,000_b$	$1,280_b$	804_b	$2,950_b$	3.4_b	211_a	104_a	$22,000_a$	$1,810_a$	418_a	35_a	21_a	370_a	$2.5E6_c$	$1.7E5_b$

*Only those subset means are shown which differ from the mean of the set of all data at the 80-percent confidence level (Student $t > 1.39$. Degrees of Freedom ≥ 10). Total number of permitted substitutions = 103. Percent Standard Error of the Mean Subscripting Code: a=0-9, b=10-19, c=20-29, d=30-39, e=40-49, f=50-62.

+Coliform counts are expressed in computer notation, i.e. $E5=10^5$.

** Average TPO_4 is $2,930_c$ and NH_4 is $2,640_c$

L_{st} = street curb-length (approximately 2.0 x street length), (curb/km, curb-miles).

3.3.2.2.2 Loading Functions for Other Pollutants

$$Y(i)_u = a \cdot Y(S)_u \cdot C(i)_u \qquad \text{(III-44)}$$

where

$Y(i)_u$ = daily total loading of pollutant i, (kg/day, lb/day) MPN per day for total coliform and fecal coliform

a = conversion factor, 10^{-6} (metric and English).

$Y(S)_u$ = daily total loading of solids, (kg/day, lb/day), calculated in Equation III-18.

$C(i)_u$ = concentration of pollutant i in solids, (ug/g); MPN/g for total coliform and fecal coliform.

Equations III-43 and III-44, along with solid loading values and compositions in Tables III-21 and III-22, provide the means to assess daily average pollutant loadings to urban street surfaces.

It is important to note that pollutant loadings so calculated are street surface loadings rather than loadings at outfalls to the receiving waters. The transport of storm runoff in sewers and removal of pollutants in some treatment systems would reduce pollutant loads to some extent. Such effects are not included in loading factors suggested in Table III-34. The use of catchment basins to remove solids and organic matter, will reduce pollutant loads from streets to receiving waters.

3.3.2.2.3 Procedure for Loading Calculations

Data in Table III-34 represent two options as well as two levels of accuracy for a user to assess pollutant loadings from a given urban area. Application of the "subset" data may result in higher accuracy, but require more data and more computation effort, than if "nationwide means" are used.

Option I - In this option the user will use nationwide means presented in Table III-21. Proceed as follows:

1. Determine solids loading rate and solids composition from tables.

2. Determine street length (include that of primary and secondary streets but not driveways, alleys, or parking lots).

3. Calculate daily solids loading using (Equation III-43).

4. Calculate daily loading of other pollutants using (Equation III-44).

Option II - In this option the user will make use of data presented for source categories in Table III-34. Steps needed for loading calculations are:

1. Characterize the study urban area. When applicable, the entire area should be divided into individual homogeneous sections with unique characteristics. Each individual section is then defined as a subarea (e.g., residential area).

1. Determine street length in each subarea.

3. Enter the Table III-34 at the line labeled "All Data."

4. Select a category of climate, land use, or average daily traffic, which best applies to an area and move upward to the line of data to the right of the category heading.

5. Substitute those values available in the row selected for the corresponding values in the row labeled "All Data." In choosing the substitute loading factors, the following priority sequence of source categories is suggested: (a) climate; (b) land use; (c) average daily traffic. The climatic zones of the U.S. delineated by the URS are shown in Figure III-15. Caution: it is not permissible to use more than one row of substitutions at a time, i.e., to use a BOD value for land use and COD for climate in order to form a new row of loading rate and composition data. It is both proper and useful, however, to repeat the above process to obtain several new rows of data to present a range of composition and loading rates.

6. Repeat Steps 4 and 5 for all subareas.

7. Use equation III-43 to calculate total solid loading in a subarea.

8. Use solid loading (Step 7), Equation III-44 and selected composition data to calculate total loading of other pollutants in a subarea.

9. Sum up loadings of subareas to obtain the loading of entire study area.

Option III - In this option, the user will make use of site specific data.

The recent URS study has assembled all presently available data on the rates of accumulation of solids and on the concentrations of various pollutant constituents in those solids that collect on street surfaces. These data are probably adequate for most urban planning operations. The user, however, may alternatively replace these loading factors by site specific data to obtain better prediction.

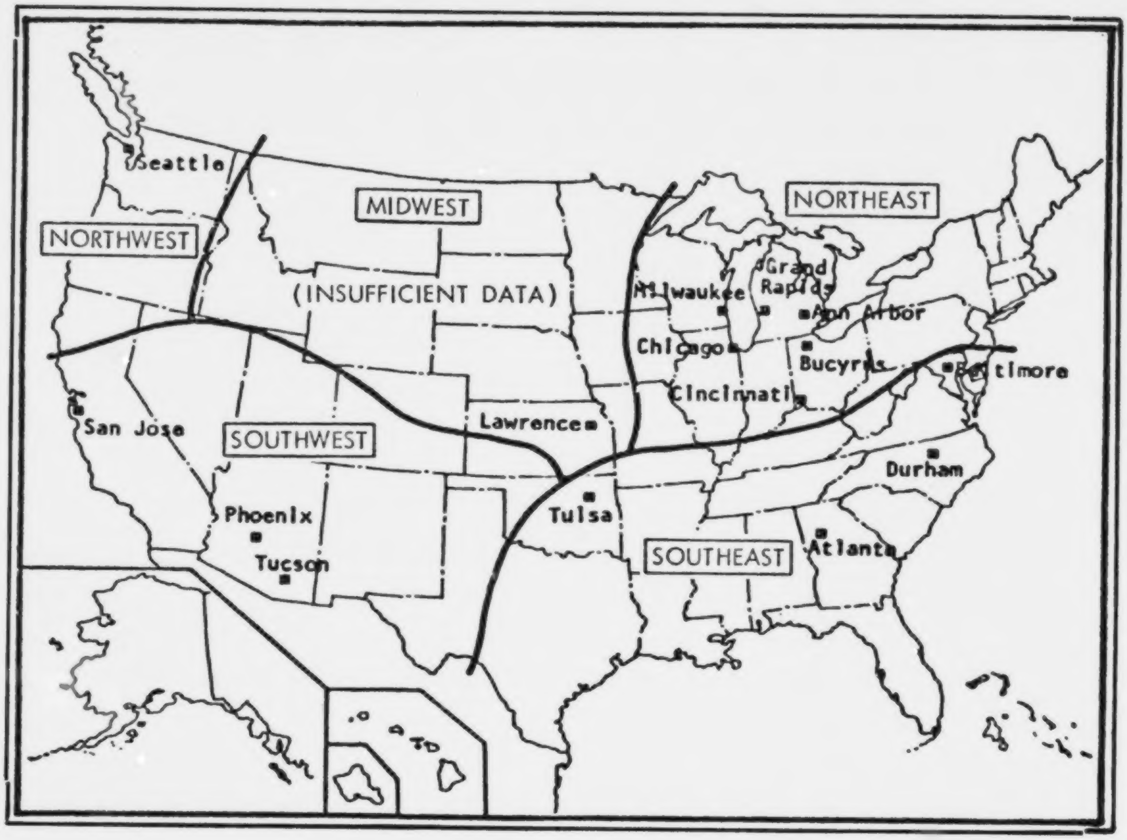
Seattle
NORTHWEST
MIDWEST
(INSUFFICIENT DATA)
NORTHEAST
Milwaukee
Grand Rapids
Ann Arbor
Chicago
Bucyrus
Baltimore
Cincinnati
San Jose
SOUTHWEST
Lawrence
Durham
Phoenix
Tulsa
Tucson
SOUTHEAST
Atlanta

Figure III-15 Climate Zone for the Cities from Which Data are Available and Used in the URS Study (Amy, et al., 1974)

If site specific data are lacking, users are encouraged to conduct sampling and analytical programs of their own. The data from site specific tests, if handled properly, may be used in analyzing the area's runoff problems instead of using values given in this report. This would be desirable in most instances, especially in areas or under specific conditions that were not documented in the URS study.

Recommended procedures for conducting site specific tests are given in Appendix B of the URS Report (Amy, et al., 1974).

With the lack of site specific data, the user may wish to examine the available published data for source and reliability. The user is referred to Appendix A of the URS Report for description of available data sources, as well as procedures for processing these data.

3.3.2.2.4 Street Length and Land Use Data for Urban Areas

Street length data are available from local public works departments or street departments. They can also be obtained by measurement of aerial photographs.

Survey statistics for the U.S. indicate that street surfaces occupy on the average about one-sixth of the urban area (Manuel, et al., 1968). The American Public Works Association (1974) recently developed a regression relationship between curb length of urban area versus population density. Data from many cities across the country were used. The resulting regression equation is:

$$CL = 413.11 - (352.66)(0.839)^{PD} \qquad \text{(III-45)}$$

where

CL = curb length density, ft/acre
PD = population density, number/acre

The correlation coefficient for the equation is 0.72. The regression curve is shown in Figure III-16.

3.3.2.3 Washoff of Pollutants to Receiving Waters

Once the equivalent load of pollutant on the watershed is known the next step is to calculate the runoff and solids loading from the storm.

The storm event runoff is found by

$$R = CR \cdot P - DS \qquad \text{(III-46)}$$

where

P = storm precipitation (inches, cm)
R = total storm runoff (inches, cm)
CR = runoff coefficient and
DS = depression storage

The runoff coefficient will be dealt with first.

3.3.2.3.1 Runoff Coefficient

In order to estimate the runoff coefficient the percent of impervious watershed area must be known. If this information is not readily available the following equation can be used for estimation:

$$I = 9.6\ PD_d^{\ (0.573\ -\ 0.391\ \mathrm{Log}_{10}\ PD_d)} \qquad \text{(III-47)}$$

where

I = percent impervious area and
PD = population density (≑ persons/acre)

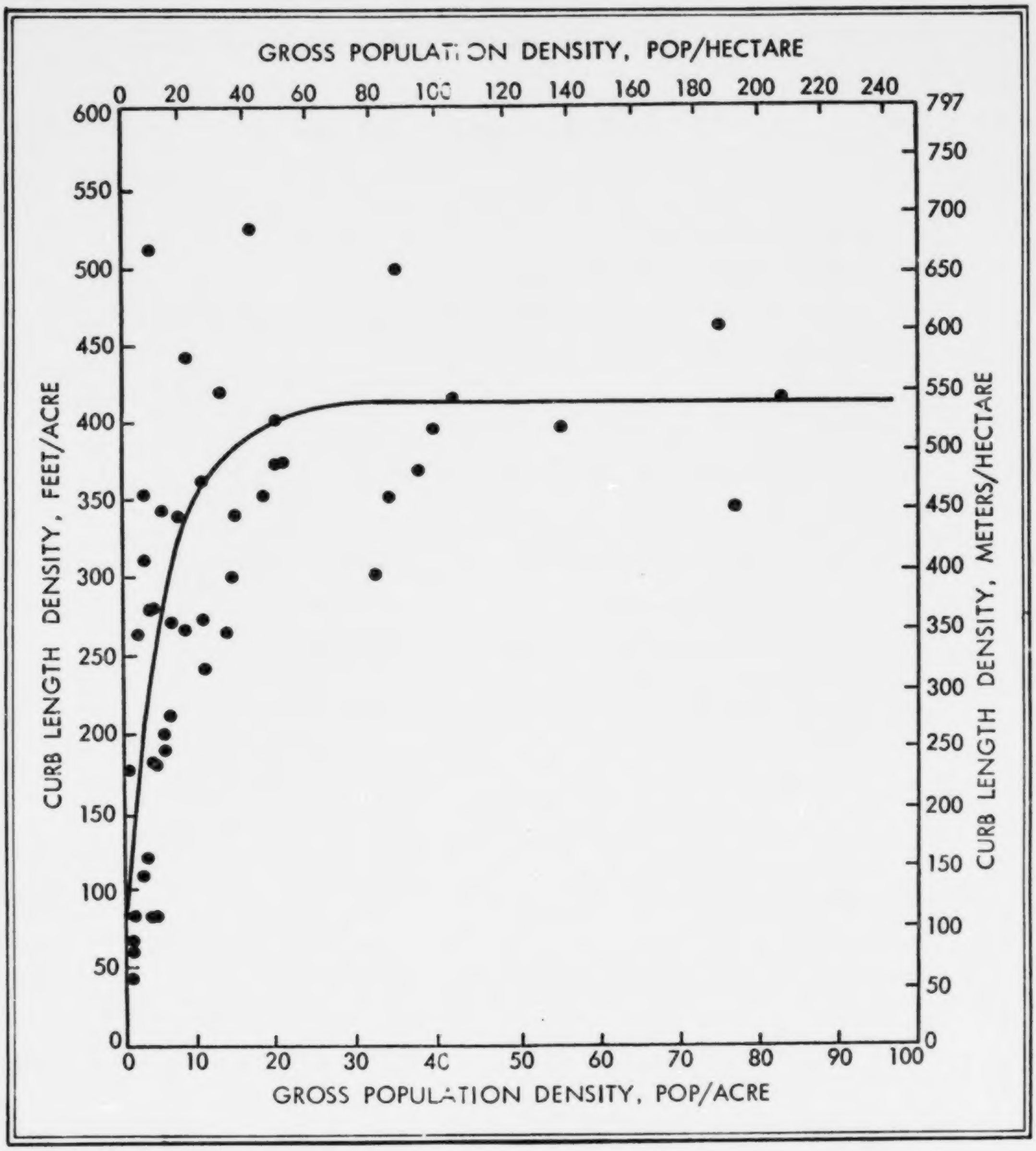

Figure III-16 Correlation Between Population Density and Curb Length Density. (American Public Works Association, 1975)

The STORM algorithm for computing the runoff coefficient is:

$$CR = 0.15 \left(1 - \frac{I}{100}\right) + K \left(\frac{I}{100}\right) \qquad \text{(III-48)}$$

where

CR = runoff coefficient

I = percent impervious area and

K = impervious area runoff coefficient based on slope information (See Table 35).

TABLE III-35

VALUES OF RUNOFF COEFFICIENT, k

Impervious Surfaces	Approximate k
Flat (< 2% slope)	0.80
Moderate (2 to 7% slope)	0.85
Steep (>7% slope)	0.90

3.3.2.3.2 Depression Storage

Depression storage on the watershed is computed as

$$DS = 0.25 - 0.1875 \left(\frac{I}{100}\right) \quad \text{English units or} \qquad \text{(III-49)}$$

$$DS = 0.63 - 0.48 \left(\frac{I}{100}\right) \quad \text{metric units} \qquad \text{(III-50)}$$

where

DS = depression storage (inches, cm)

3.3.2.3.3 Solids Removal

Once the total storm runoff has been computed the percentage of solids removed from the street surfaces can be estimated by referring to the graph in Figure III-17. The solids load for the runoff event is

$$Y(S)_w = EDA \cdot Y(S)_u \cdot (PC) \tag{III-51}$$

when

$Y(S)_w$ is the load of solids removed to the receiving water body (lbs, kg)

EDA is the equivalent number of days of accumulation

$Y(S)_u$ is the street surface loading rate (lb/day, kg/day) and

(PC) is the percentage (expressed as a decimal fraction) of solids removed during the storm event

The user should realize that the runoff coefficient and hence the stream loading rate does not incorporate the effects of losses in sewers or stormwater detention basins. For more accuracy in these complex situations the user is directed toward a more sophisticated urban stormwater model which would require a hydraulic description of these structures.

3.3.2.3.4 Other Pollutants

As in the street surface loading equation the quantity of other pollutants is determined by a product of a concentration factor and the loading of solids. Factors for several conventional pollutants and some metals can be found in Table III-34.

Smolenyak (1979) developed loading equations for other conventional pollutant forms given the suspended solids load. His coefficients for linear and power function models are given in Table III-36. These

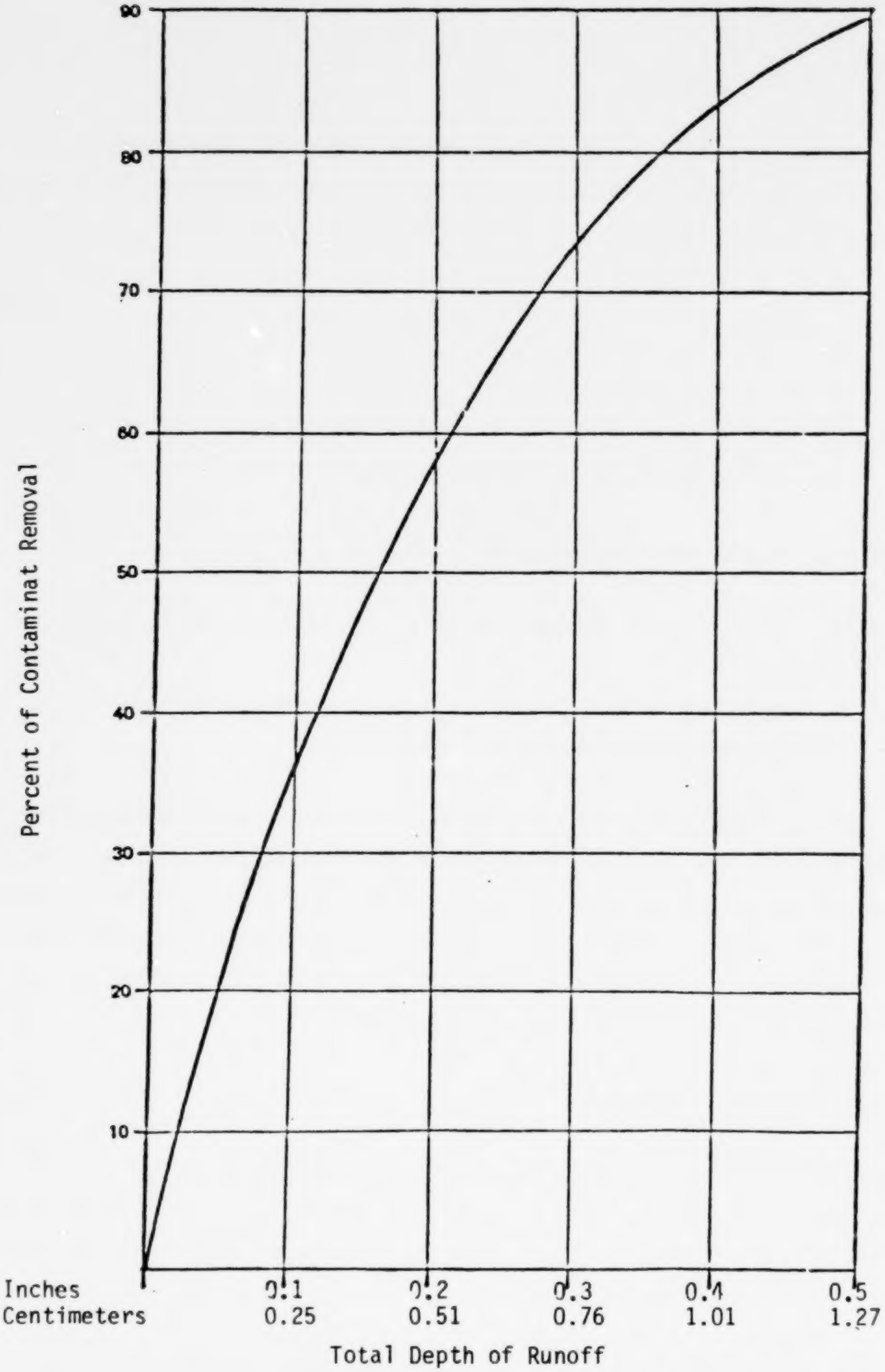

FIGURE III-17 STREET SURFACE CONTAMINANT REMOVAL AS A FUNCTION OF RUNOFF

Source: Amy, et al., 1974

TABLE III-36

RELATIONSHIPS BETWEEN TOTAL SUSPENDED SOLIDS (TSS) AND OTHER POLLUTANTS

Dependent Variable	No. of Events	Linear (Load = a+b · TSS			Log-Log (Load = aTSS^b)		
			Reg. Coef.			Reg. Coef.	
		R^2	a	b	R^2	a	b
BOD	76	.18	24	1.7	.42	.39	.99
COD	109	.52	3.4	.19	.73	.92	.72
NH_4^+	20	.41	.065	.0027	.18	.022	.48
NO_3^-	20	.43	.007	.0012	.54	.0046	.60
NO_2 + NO_3^-	100	.14	.011	.00077	.57	.0071	.55
Organic N	38	.67	.072	.0029	.83	.011	.80
Total N	14	.83	.0083	.0027	.75	.0075	.78
Dissolved PO_4-P	31	.22	.0081	.00014	.65	.0010	.67
Total PO_4	113	.06	.003	.00017	.65	.0012	.68
Total P-P	28	.25	.084	.028	.68	.0041	1.2

regressions were performed on combined data from 23 different urban catchments in various U.S. cities.

3.3.2.4 Toxic Pollutant Accumulation

Toxic pollutants in urban watersheds are introduced by a variety of activities. Atmospheric deposition from industrial emissions and vehicular emissions are primary sources. Other sources include spills onto highways and loading docks. Such spills may represent significant loads of toxicants because they generally occur onto impervious surfaces.

The discussion of deposition of toxic pollutants to urban areas will be divided into two categories

1. metals and
2. organic pollutants

3.3.2.4.1 Deposition of Metals

The loading of metals to street surfaces is estimated in the same manner as for conventional pollutants. The product of equivalent days of accumulation, solids loading rates and concentration factor for the metals in solids (Table III-34) is used.

EXAMPLE III-6

Estimation of Lead Washoff Load for a Single Storm Event

Estimate the amount of lead removed from the street surface of Laurel, MD, during a single storm event. The rainfall depth of the storm is 1.21 inches. The population density for Laurel is 13.2 persons acre^{-1} and there are 70 curb-miles in the town. When the storm occurred, it had been eight days since the last significant rainfall and four days since the streets had been swept. (Sweeping efficiency = 0.750) Use a solids supply rate of 103-lb/day curb-mile.

Solution

First determine the percent impervious area using Equation III-47

$$I = 9.6\ (PDd)^{(0.573\ -\ 0.0392\ \log_{10}\ Pdd)}$$
$$PDd = 13.2 \text{ and}$$
$$I = 37.6 \text{ percent}$$

Next, compute the runoff coefficient for the area using Equation III-48

$$CR = 0.15\ (1 - \frac{1}{100}) + 0.85\ (\frac{1}{100})$$
$$I = 37.6 \text{ and}$$
$$CR = 0.41$$

The depression storage is computed as (Equation III-49)

$$DS = 0.25 - 0.1875\ (I/100)$$
$$I = 37.6$$
$$DS = 0.18$$

The storm runoff can now be computed by Equation III-46 as

$$\begin{aligned} Q &= CR \cdot P - DS \\ &= 0.41\ (1.21) - 0.18 \\ &= 0.32 \text{ inches} \end{aligned}$$

Now, the supply of solids which is present on the watershed must be determined. Compute the equivalent days of accumulation (EDA) as (Equation III-42)

$$\begin{aligned} EDA &= (D_r - D_s)\ (1 - \varepsilon_s) + D_s \\ &= (8 - 4)\ (1 - 0.75) + 4 \\ &= 5 \text{ days} \end{aligned}$$

Using a solids loading rate of 103 lb/curb-mile - day, Equation III-43 gives

$$Y(S)_u = 103 \cdot (70) = 7210 \text{ lb/day}$$

Equation III-44 gives the amount of lead deposited per day as a function of solids

$$\begin{aligned} Y(i)_u &= 10^{-6} (7210)(1370) \\ &= 9.9 \text{ lb - Pb/day} \end{aligned}$$

Since the washoff of lead as opposed to solids is of concern, the Y(S) becomes $Y(i)_w$ in Equation III-51 and

$$\begin{aligned} Y(i)_w &= 5\ (9.9)(.75) \\ &= 37.1 \text{ lb - Pb} \end{aligned}$$

washed off in the event.

END OF EXAMPLE III-6

3.3.2.4.2 Deposition of Organic Pollutants

Many pollutants are discharged into the atmosphere and eventually settle out directly onto water surfaces, or onto the watershed surface where they become available for transport. Pollutants occur in the atmosphere as 1) particulates; 2) gases; or 3) dissolved in water vapor. Eisenreich et al. (1981) have suggested that compounds having saturation vapor pressures (P_s) of 10^{-8} will primarily be particulate whereas those compounds with $P_s > 10^{-4}$ will be primarily in the vapor phase. Cautreels and Van Cauwenberghe (1978) give distribution coefficients between the gas and particulate phases for 55 aliphatic hydrocarbons, PAH's, phthalic acid esters, fatty acid esters, aromatic acids and basic compounds.

Both particulates and gases may settle out onto receptor surfaces. For particles <0.3 μm in diameter, the major process is Brownian diffusion for diameters 0.5 to 5 μm inertial impaction-interception governs and for diameters >5 μm, gravitational settling is dominant. For gravitational settling, Stokes' Law may be used to predict the settling velocity. Since Stokes' Law is applicable only to quiescent media, it should give an upper bound for V_d (the deposition velocity). It is stated as

$$V_d = \frac{g(ad)^2}{18\mu}(\rho - \rho_a) \qquad \text{(III-52)}$$

where

V_d = settling velocity (cm/sec)
a = conversion factor (10^{-4})
g = acceleration of gravity, 981.46 (cm/sec^2)
μ = viscosity of air, 0.000177 (g/cm-sec) at 50°F (10°C)
ρ = particle density, ~ 2 (g/cm^3)
ρ_a = density of air, 0.001243 (g/cm^3) at 50°F (10°C)
d = particle diameter (microns)

For particles <5 µm in diameter Stokes Law is not applicable and experimental values for the deposition velocity should be used. Eisenreich et al. (1981) suggest values of V_d = 0.1 to 0.5 cm/sec for trace organics. Some experimental values are shown in Table III-37.

Once the settling velocity is known, the following procedure can be used to predict the dry deposition loadings:

$$L = V_d \cdot C_p \cdot A \cdot f \qquad \text{(III-53)}$$

where

L is the load of the pollutant delivered to the receptor surface as dry deposition (appropriate mass units/sec)
V_d is the particle settling (deposition) velocity (m/sec)
C_p is the concentration of atmospheric particulates (mass/m^3)
A is the projected receptor ares (m^2)
f is the fraction (by weight) of the pollutant in the particulates

Normally, smaller size particles are more chemically and physically reactive than larger particulates, and therefore pollutants will be associated with these smaller particles. Obviously the particle size to which pollutants are adsorbed affects their atmospheric residence time and, hence, loadings. According to Neff (1979), most PAH are associated with

TABLE III-37

FIELD-MEASURED DRY DEPOSITION VELOCITIES

Compound	V_d (cm/s)	Collection Surface
PCB (Aroclor 1242, 1254)	0.5	---
PCB	0.3-3	Mineral-oil-coated plates
PCB, DDT (gas phase)	0.19	Estimated
PCB, DDT	1.0	Estimated
PCB (total)	0.14	Glycerol-coated plates
PCB (Aroclor 1016)	0.04	Glycerin-water, Al pans
PCB	0.43	---

Source: Eisenreich _et al._, 1981

particulates in the 1 to 2 micron range. Van Vaeck and Cauwenberghe (1978) have shown that aerosol PAH are associated with particles of median diameter from 0.7 to 1.4 μm. In addition, they give the concentrations of 50 trace organic compounds associated with different size particles. Higher weight PAH, alkanes, and carboxylic acids had significant mass fractions associated with >1 μm diameter particles.

EXAMPLE III-7

Dry Atmospheric Deposition of Pollutants Adsorbed to Particulates

Estimate the maximum daily loading of pyrene to a watershed having an area of $10^6 m^2$ overlain by an air mass having a mean daily particulate concentration of 50 $\mu g/m^3$. The average pyrene content of the particulates is 1.0×10^{-4} μg-pyrene/μg. Assume a deposition velocity of 0.1 cm/sec.

Solution:

Compute the daily dry deposited load of pyrene.

$$\begin{aligned} L &= V_t \cdot C_p \cdot A \cdot f \\ &= 0.001 \frac{m}{sec} \cdot \frac{50\ \mu g}{m^3} \cdot 10^6 m^2 \\ &\quad \cdot 1.0 \times 10^{-4} \frac{\mu g\ pyrene}{\mu g} \quad \frac{86400\ sec}{day} \\ &= \underline{\underline{4.32 \times 10^5}}\ \mu g/day \end{aligned}$$

Ans.

END OF EXAMPLE III-7

Gas phase pollutants may also be deposited directly to the watershed surface. In this case the loading equation is

$$L = V_d \cdot C \cdot A \qquad \text{(III-54)}$$

where

L is the dry deposited load (mass/sec)
V_d is the gas deposition velocity (m/sec) and
A is the receptor area (m^2)
C is the ambient concentration of the gas phase pollutant.

EXAMPLE III-8

Dry Atmospheric Deposition of Gaseous Pollutants of Gaseous Pollutants

Estimate the annual deposition of toxaphene to a 1 Km area at Stoneville, MS during 1974. The mean monthly atmospheric concentrations are shown in Table III-42. Assume an average deposition velocity of 0.2 cm/sec for the entire year.

Solution:

$$L = \sum_{n-1}^{12} V_d \cdot C_n \cdot A \cdot \Delta t_n$$

	Vd (m/sec)	C_n (ng/M³)	A (M²)	t_n	L
1	.002	10.9	10^4	31 x 86400	5.84×10^8
2	.002	9.7	10^4	28 x 86400	4.69×10^8
3	.002	19.1	10^4	31 x 86400	1.02×10^9
4	.002	27.7	10^4	30 x 86400	1.43×10^9
5	.002	44.3	10^4	31 x 86400	2.37×10^9
6	.002	38.6	10^4	30 x 86400	2.00×10^9
7	.002	175.0	10^4	31 x 86400	9.37×10^9
8	.002	903.6	10^4	31 x 86400	4.84×10^{10}
9	.002	524.6	10^4	30 x 86400	2.72×10^{10}
10	.002	114.8	10^4	31 x 86400	6.15×10^9
11	.002	32.9	10^4	30 x 86400	1.71×10^9
12	.002	12.6	10^4	31 x 86400	6.75×10^8
					1.01×10^{11} ng/year

or 101.4 g/year Ans.

In actual situations the deposition velocity changes with meteorological conditions especially wind speed. In general, deposition velocities diminish as wind speeds decrease. Further reading on gaseous pollutant deposition can be found in Murphy et al. (1980).

END OF EXAMPLE III-8

Precipitation falling through the atmosphere tends to scavenge particulates and absorb gases so that it contains a variety of substances. Because of the volume of precipitation which generally occurs, it may constitute a significant source of pollutant loading to the watershed surface. Load calculation for wet deposition is shown below:

where

$$L = 10 \cdot C \cdot P \cdot A \qquad \text{(III-55)}$$

L is the load of the pollutant delivered to the receptor as wet deposition (appropriate mass units/sec)

C is the concentration of the pollutant in precipitation (mass/liter)

P is the precipitation rate (cm/sec)

A is the projected receptor area (m^2)

If concentrations of constituents in rainwater are unknown, they can be estimated using the ambient vapor phase concentrations of the pollutant and the Henry's Law constant for the pollutant. By assuming equilibrium between the gas and water phases, one can write

$$C_l V_l + C_g V_g = C_t V_t \quad \text{or} \qquad \text{(III-56)}$$

$$C_1 = \frac{C_t \left(\frac{V_g}{V_1} + 1\right)}{\frac{V_g}{V_1} H + 1} \qquad \text{(III-57)}$$

where

C_1 is the concentration of the pollutant in water $\mu g/m^3$
V_1 is the volume of rainfall m^3
C_g is the concentration in the gas phase ($\mu g/m^3$)
V_g is the gas phase volume (m^3)
C_t is the total pollutant concentration $\mu g/m^3$
V_t is the total volume of the atmosphere (m^3) and
H is the Henry's Law constant for a particular pollutant.

Because $HV_g >> V_1$ for almost all of the priority pollutants and $V_g \sim V_t$ the equation reduces to

$$C_1 = \frac{C_t}{H} \qquad \text{(III-58)}$$

Thus for toluene, for instance, if C_t is 1 $\mu g/m^3$ air

$$C_1 = \frac{1.0}{.27}$$

$$= 3.7 \ \mu g/m^3 \text{ water}$$

For Henry's Law constants on the order of 10^{-6} the equation for C_1 can be rewritten as

$$C_1 = \frac{C_t \cdot \left(\frac{W_g}{W_1} \frac{\rho_1}{\rho_g} + 1\right)}{H \cdot \frac{W_g}{W_1} \cdot \frac{\rho_1}{\rho_g} + 1} \qquad \text{(III-59)}$$

where

ρ_g is the gas density
ρ_1 is the water vapor density

W_1 is the weight of water vapor in the atmosphere and
W_g is the weight of dry air.

W_g, W_1, ρ_g, and ρ_1 can be determined for any temperature and relative humidity from a standard psychrometric chart.

Another similar approach to determining wet deposition is the use of washout rations (Eisenreich et al., 1981). The wet flux is calculated by

$$F = W_i \cdot I \cdot C_a \qquad \text{(III-60)}$$

where

F is the wet pollutant flux ($MT^{-1}L^{-2}$)
W_i is the washout ratio for pollutant i
I is the precipitation rate (LT^{-1}) and
C_a is the ambient pollutant concentration (ML^{-3}).

Calculated and observed valued of W_i for some contaminants are shown in Table III-38. Note that field measured washout ratios contain the effect of particulate scavenging by rainfall whereas calculated values only consider constituents absorbed as gases from the atmosphere.

In order to use the methods for determining dry and wet deposition and gaseous absorption, the atmospheric concentration of the pollutant must be known. For the 129 priority substances, very little monitoring data is available. Some scattered data are available such as that in Tables III-39 through 42. For a particular locale, some monitoring will need to be done at this stage.

3.3.2.5 Washoff of Toxic Pollutants

The amount of organics or metals lost in solids or dissolved phase is estimated using the adsorption partition coefficient. The fractions are given by

TABLE III-38

WASHOUT RATIOS FOR SELECTED TRACE ORGANICS

Compound	$RT/H = W_i$	W_{field}
Dieldrin	1.1×10^5	$2\text{-}9 \times 10^3$
Aldrin	1.6×10^3	
DDT	5.9×10^2	$2\text{-}8 \times 10^4$
HCH	5×10^4	$1\text{-}5 \times 10^4$
Aroclor 1242	4×10^1	1×10^4
Aroclor 1248	6.3	9×10^4
Aroclor 1254	8.3	$2\text{-}9 \times 10^4$
	$8\text{-}35 \times 10^4$	
Aroclor 1260	2.9	--
Hexachlorobenzene	3.7×10^2	1.5×10^3
Chloroterpenes	3.5×10^4	7×10^3- 3×10^5
Di-2(ethylhexyl) phthalate	--	$1\text{-}9 \times 10^4$

Source: Eisenreich _et al_., 1981

Note: H (Henry's law constant) in this table has units of liter-atm/mole. Essentially $W_i = \frac{1}{H}$ as defined previously.

TABLE III-39

PCB's, DDT's, AND PHTHALATE ESTERS IN THE GULF OF MEXICO ATMOSPHERE*

Sample No.	Date	Concentration (ng m^{-3}) PCB	 p,p´-DDT	 p,p´-DDE	 DEHP	 DBP
1	3/26-27	0.66	0.042	0.116	1.92 (51)	3.71 (68)
2	3/28-29	0.37	0.078	0.065	0.72 (67)	0.84 (94)
3	3/29-30	0.17	0.047 (90)	0.026	1.45 (51)	3.34 (20)[a]
4	3/30-31	0.18	0.020	0.018	1.75 (78)	0.65 (88)
5	3/31-4/1	0.13[b]	0.016[b]	0.010[b]	0.53[b](--)	0.75[b](--)
6	4/1-2	0.17	0.022	0.009	1.72 (71)	1.03 (45)
7	4/2-3	0.23	0.041	0.018	1.34 (50)	0.16[c](--)
8	4/3-4	0.71	0.021	0.017	1.80 (25)	1.30 (46)
9	4/4-5	0.79	0.044	0.180	1.34 (69)	0.80 (66)
10	4/6-7	0.35	0.010	0.031	0.83 (58)	0.38[c](--)
Average		0.35	0.034	0.049	1.16 (57)	1.30 (68)

[a] Questionable value, not included in average.

[b] Vapor phase only

[c] Particulate only.

[*] Concentrations (in ng m^{-3}) are for the total sample. The numbers in parentheses are the percent of the compound measured in the vapor phase only. Unless otherwise indicated all PCB's, DDT, and DDE vapor concentrations are >98%.

Source: Giam et al., 1980.

TABLE III-40

1975 MONTHLY AVERAGE CONCENTRATIONS OF THREE ORGANIC COMPOUNDS AT THREE NEW YORK CITY LOCATIONS

Month	TSPM* Micrograms/m³			DBP* Nanograms/m³			DEHP* Nanograms/m³			BEO* Micrograms/m³		
	Sector			Sector			Sector			Sector		
	23	27	34	23	27	34	23	27	34	23	27	34
January	85.43	59.52	63.71	4.90	4.93	3.87	10.89	11.96	18.58	3.87	3.08	4.15
February	NDA	61.21	NDA	NDA	8.49	NDA	NDA	15.41	NDA	NDA	4.13	NDA
March	47.39	52.71	56.63	2.93	5.03	4.33	10.91	12.30	13.06	1.76	2.56	2.54
April	53.42	70.31	65.72	3.00	4.84	2.72	4.93	12.48	13.50	1.88	2.96	2.54
May	NDA	89.38	68.58	NDA	3.17	2.22	NDA	14.72	12.23	NDA	3.89	2.67
June	NDA	67.28	67.25	NDA	1.99	1.80	NDA	10.06	11.02	NDA	2.39	2.06
July	NDA	74.41	56.97	NDA	3.48	0.14	NDA	14.05	8.96	NDA	3.84	1.63
August	NDA	63.51	55.34	NDA	5.00	1.80	NDA	15.48	13.58	NDA	3.45	1.87
September	57.19	54.74	51.67	4.40	4.79	7.38	8.81	17.93	12.15	1.43	3.04	3.26
October	98.78	73.65	73.64	2.98	10.28	2.81	12.15	28.60	22.15	3.98	5.24	3.53
November	69.53	65.69	79.74	4.15	5.31	5.69	13.52	23.24	16.76	3.79	5.01	3.56
December	NDA	57.96	NDA	NDA	10.99	NDA	NDA	25.30	NDA	NDA	5.66	NDA
Average Urban		65.86			4.41			14.45			3.21	
Suburban (Sterling Forest, N.Y.)					1.41			2.51				

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*TSPM, Total Suspended Particulate Matter; DBP and DEHP, di-Butyl and di-(2-Ethylhexyl) phthalate; and BEO, Benzene Extractable Organics.

Source: Bave et al, 1978.

TABLE III-41

SEASONAL FLUCTUATIONS IN THE GEOMETRIC MEAN PAH CONCENTRATIONS IN AIR SAMPLES COLLECTED AT 13 STATIONS IN THE LOS ANGELES, CALIFORNIA, AREA

Compound	Quarter concentration (ng/m³)			
	1	2	3	4
Pyrene	0·58	0·23	0·25	1·24
Fluoranthene	0·38	0·15	0·24	0·68
Benz[a]anthracene	0·30	0·06	0·10	0·59
Chrysene	0·70	0·26	0·44	1·57
Benzo[e]pyrene	1·30	0·42	0·62	1·96
Benzo[a]pyrene	0·77	0·17	0·26	1·27
Benzo[b]fluoranthene		0·24	0·33	1·30
Benzo[i]fluoranthene	0·26	0·06	0·12	0·43
Benzo[k]fluoranthene	0·27	0·07	0·15	0·52
Perylene	0·22		0·06	0·22
Anthanthrene	0·33	0·08	0·14	0·79
Benzo[ghi]perylene	3·80	1·35	2·71	8·25
Indeno[1,2,3-cd]pyrene	1·79	0·68	1·00	2·64
Coronene	2·49	1·13	1·66	4·44
Total PAH measured	13·19	4·90	8·08	25·90

Source: Neff, 1979

TABLE III-42

AVERAGE MONTHLY ATMOSPHERIC LEVELS OF FOUR PESTICIDES AT STONEVILLE, MISSISSIPPI

	Endrin (ngm^{-3})			Toxaphene (ngm^{-3})		
	1972	1973	1974	1972	1973	1974
January	1.1	0.1	0.2	0.0	0.0	10.9
February	1.1	0.1	9.2	13.0	0.0	9.7
March	2.1	0.7	0.6	68.0	16.8	19.1
April	3.1	0.7	0.5	67.4	10.8	27.7
May	1.0	1.2	0.7	32.4	46.8	44.3
June	0.9	3.8	0.7	44.2	109.9	38.6
July	5.2	0.7	9.3	400.7	41.1	175.0
August	10.1	5.0	27.2	1540.0	268.8	903.6
September	8.8	8.4	18.8	827.9	322.6	524.6
October	4.0	5.0	4.3	97.9	161.1	114.8
November	0.5	1.1	1.0	9.3	0.0	32.9
December	0.0	0.2	0.5	0.0	9.9	12.6
Average	3.2	2.3	5.3	258.4	82.3	159.5
	Methyl Parathion (ngm^{-3})			Total DDT (ngm^{-3})		
January	0.0	0.0	1.0	10.8	3.9	3.0
February	0.0	0.0	0.3	12.6	4.8	3.6
March	0.0	0.0	0.3	32.6	11.1	7.6
April	0.0	0.0	0.6	34.1	11.4	7.7
May	0.0	0.0	0.6	17.2	18.6	15.6
June	1.6	22.8	0.9	16.2	49.5	12.8
July	61.4	4.5	40.9	117.3	9.6	24.3
August	216.9	129.3	341.1	515.3	25.6	37.9
September	111.7	791.1	167.9	378.8	24.6	19.4
October	1.4	17.1	2.0	37.6	18.9	5.1
November	0.0	0.0	0.0	14.8	11.9	3.3
December	0.0	0.1	0.0	6.3	2.4	2.1
Average	32.8	80.4	46.3	99.5	16.0	11.9

Source: Arthur *et al*, 1976

$$F_w = [1 + \rho_s K_d]^{-1} \quad \text{(III-61)}$$

$$F_s = [1 + \frac{1}{\rho_s K_d}]^{-1} \quad \text{(III-62)}$$

where

F_w = fraction of dissolved pollutant
ρ_s = sediment concentration (g/cm^3)
K_d = adsorption partition coefficient (cm^3/g) and
F_s = the fraction of sorbed pollutant

The average sediment concentration ρ_s is determined by dividing the sediment loss by the total storm runoff

$$\rho_s = a \cdot Y(S)_w / (A_w \cdot Q) \quad \text{(III-63)}$$

A_w = watershed area (ha, ac)

when

ρ_s	is the suspended sediment concentration (g/cm^3, lb/ft^3)
$Y(S)_w$	is the sediment load (kg, lb)
Q	is the total storm runoff depth (in, cm)
a	is a conversion constant $= 10^{-5}$ metric $= 2.75 \times 10^{-4}$ English

$Y(S)_w$ and Q are determined by urban runoff single event procedures in section 3.3.2.3.

Tables III-43 and III-44 show the relative magnitudes of concentrations of metals and some organic pollutants in wet and dry weather flows. Wet/dry ratios show that the concentration of metals in nonpoint source runoff is from 1 to 10 times greater than dry weather flows in which the contributions are primarily from point sources. Concentrations of PAH are 100 times greater from nonpoint than point sources.

TABLE III-43

FLOW WEIGHTED MEAN CONCENTRATIONS OF TRACE METALS AND CHLORINATED HYDROCARBONS IN THE LOS ANGELES RIVER (µg/l)

	1971-1972			1979-1980		
Constituent	Dry Weather Flow	Storm Runoff	Ratio Wet/Dry	Dry Weather Flow	Storm Runoff	Ratio Wet/Dry
Ag	1.4	2.2	1.6	0.4	0.8	2.0
Cd	4.3	13.	3.0	6.2	4.0	0.64
Cr	84.	83.	.99	30.	100.	3.3
Cu	21.	130.	6.2	52.	87.	1.7
Hg	0.39	1.0	2.6	0.25	0.8	3.2
Ni	24.	78.	3.2	43.	61.	1.4
Pb	150.	940.	6.3	56.	160.	2.9
Zn	230.	100.	.43	200.	960.	4.8
Fe*	3.8	18.	4.7	4.8	51.	10.6
Mn	120.	480.	4.0	130.	650.	5.
DDT	0.27	0.93	3.4	0.05	0.33	6.6
PCB	1.6	2.6	1.6	0.21	0.31	1.5

*mg/l

Source: Coastal Water Research Project Biennial Report 1979-1980.

TABLE III-44

CONCENTRATIONS OF PAH IN MUNICIPAL WASTEWATER EFFLUENTS IN THE GFR (ALL VALUES ARE IN THE μG/LITER)

Compound	Dry Weather	During Heavy Rain	Ratio Wet/Dry
Fluoranthene	0.352	16.350	46.4
Pyrene	0.254	16.050	62.2
Benz[a]anthracene	0.025	10.360	414.4
Benzo[b]fluoranthene	0.039	10.790	276.7
Benzo[i]fluoranthene	0.057	9.910	173.9
Benzo[k]fluoranthene	0.022	1.840	83.6
Benzo[a]pyrene	0.001	3.840	3840.0
Benzo[ghi]perylene	0.004	4.180	1045.0
Indeno[1,2,3-cd]pyrene	0.017	4.980	292.9
Total identified PAH	0.771	78.300	
Total unidentified PAH	0.075	9.200	
Total PAH	0.846	87.500	103.4

Source: Neff, 1979

Washoff of Organic Urban Pollutants

Estimate the washoff of pyrene from the street surface of Laurel, MD during the storm in Example III-6. Assume the deposition rate of pyrene from Example III-7. Estimate the load of pyrene in runoff (dissolved) and adsorbed to solids. The K_{OC} for pyrene is approximately 1.2×10^5 and the streets solids are 20 percent organic carbon.

Solution:

From problem III-6

A_w = 1000 ha

EDA = 5

Q = 0.32 in or 0.81 cm

$Y(S)_u$ = 7210 lb/day or 3277 kg/day

$Y(\text{pyrene})_u = 4.3 \times 10^5$ ug/day

The washoff of solids is (Equation III-51)

$$Y(S)_u = 5\ (3277)(.75)$$
$$= 12289 \text{ kg-solids}$$

The mean concentration of solids is (Equation III-63)

$$\rho_s = 10^{-5}(12289)(0.81 \cdot 1000)$$
$$= 0.15 \text{ kg/m}^3 \text{ or } 1.5 \times 10^{-4} \text{ g/cm}^3$$

To estimate the K_d (partition coefficient) for pyrene Equation III-30 can be used

$$K_d = \frac{1.2 \times 10^5 (20)}{100}$$
$$= 24000 \text{ cm}^3/\text{g}$$

Using Equations III-61 and III-62 the dissolved and adsorbed pyrene fractions are

$$F_w = [1 + (1.5 \times 10^{-4})(24010.)]^{-1}$$
$$= 0.22 \qquad \text{and}$$

$$F_s = \left[1 + \frac{1}{1.5 \times 10^{-4}(24000)}\right]^{-1}$$

$$= 0.78$$

The dissolved and adsorbed loads are the product of the above fractions and the total pyrene load (Equation III-51)

$$Y(\text{pyrene})_W = 5(4.3\text{x}10^5)(.75)$$
$$= 1.6\text{x}10^6\ \mu\text{g}$$

$$Y(\text{pyrene})_{W_W} = F_W\ 1.6\text{x}10^6$$
$$= 0.22(1.6\text{x}10^6)$$
$$= 3.5\text{x}10^5\ \mu\text{g}$$

$$Y(\text{pyrene})_{W_S} = F_S\ (1.6\text{x}10^6)$$
$$= 0.78\ (1.6 \times 10^6)$$
$$= 1.25\text{x}10^6\ \mu\text{g}$$

Note that although the partition coefficient for pyrene is very high, a substantial quantity of pyrene is in the dissolved form (22 percent). This is due to the very low mean solids concentration (only 150 mg/l). The mean pyrene concentration is about 0.20 µg/l which is close to dry weather values in Table III-46.

END OF EXAMPLE III-9

3.4 POINT SOURCE WASTE LOADS

The purpose of this section is to discuss sources of information concerning point source discharges and to provide a reasonable range of values for discharge concentrations when no direct source data can be located. When available, direct data concerning an existing or proposed discharge is preferable to the use of the information presented here.

3.4.1 Direct Sources of Data

Before using these guidelines and estimates a planner should exhaust the sources of actual point source waste loading information available to him. The discharger may be the best source of information since many states require dischargers to maintain a self monitoring program. Pollutant load per day and pollutant concentration data are usually included in this information. Second, essentially all point source discharges are required to obtain a discharge permit. The state or federal agency issuing these permits will have on file maximum allowable limits for the discharge. These limits can be used as an upper bound waste loading rate. Third, state water quality or water resource agencies often have conducted sample collection programs for significant discharges. Fourth, data for a similar facility within the local region (same activity, same general size) may be used as an estimate for an unknown waste load. If none of these are available the following procedure may be used.

3.4.2 Estimation of Municipal Waste Loads

The equation for estimating municipal waste loads is shown below. Basically this method involves computing an influent load and reducing that load according to removal efficiency based on treatment type. The equation is

$$Y(P)_m = Q_p \cdot P_p \cdot C_m \cdot (1-\varepsilon) \cdot 10^{-9} \qquad \text{(III-64)}$$

where

$Y(P)_m$ is the waste load being delivered from the treatment plant to the stream (Kg/day)
Q_p is the flow per capita per day
P_p is the population being served by the treatment facility
C_m is the concentration of a particular pollutant in raw domestic sewage (μg/l) and
ε is the removal efficiency based on treatment type.

3.4.2.1 Evaluation of Parameters in the Municipal Waste Loading Equation

The utilization of domestic water depends on a number of factors. Among them are:

- geographic location
- climate
- degree of industrialization and
- size of community

A reasonable estimation of water comsumption in different parts of the country is found in Table III-45. Average water consumption per capita by state and selected municipalities are shown. The user should note the large variations in the table. These rates can be used for the parameter Q_p if more site specific data is unavailable.

Typical concentrations of conventional wastewater constituents in untreated domestic wastewater (mg/l) is shown in Table III-46. If the relative strength of the raw sewage is unknown, use of the higher values are recommended.

Removal efficiencies vary greatly depending upon the constituent and upon treatment process. Typical removal efficiencies are shown in Table III-47.

An example of the differences in loadings of untreated and treated domestic sewage are shown in Table III-48.

3.4.3 Industrial Waste Loads

Industry is a source of many types of pollutants. Of the conventional pollutants, they are primarily sources of BOD, suspended solids, COD, and oil and grease. They are also primary sources of toxic organic pollutants and metals as will be discussed in the next section.

TABLE III-45

WATER WITHDRAWALS FOR PUBLIC SUPPLIES BY STATES AND BY SELECTED MUNICIPAL SYSTEMS, 1970

State, city	L/ capita·d	gal/ capita·d	State, city	L/ capita·d	gal/ capita·d	State, city	L/ capita·d	gal/ capita·d
Alabama:	806	213	Maine:	553	146	Oklahoma:	492	130
Birmingham	576	152	Portland	580	153	Tulsa	595	157
Alaska:	1790	473	Maryland:	515	136	Oregon:	712	188
Anchorage	769	203	Baltimore	648	171	Portland	1129	298
Arizona:	787	208	Massachusetts:	530	140	Pennsylvania:	685	181
Phoenix	864	228	Boston	883	233	Pittsburgh	485	128
Arkansas:	503	133	Michigan:	636	168	Rhode Island	462	122
Little Rock	784	207	Detroit	671	177	South Carolina:	916	242
California:	685	181	Minnesota:	473	125	Charleston	652	172
Los Angeles	686	181	St. Paul	515	136	South Dakota:	549	145
San Francisco	1424	376	Mississippi:	507	134	Sioux Falls	587	155
Colorado:	746	197	Jackson	432	114	Tennessee:	488	129
Denver	955	252	Missouri:	485	128	Memphis	549	145
Connecticut:	541	143	Kansas City	587	155	Texas:	587	155
Hartford	564	149	Montana:	826	219	Dallas	610	161
Delaware	700	85	Billings	754	199	Houston	947	250
Florida:	617	163	Nebraska:	636	168	Utah:	1113	294
Miami	1208	319	Omaha	742	196	Salt Lake City	523	138
Georgia:	946	250	Nevada:	1154	305	Vermont	553	146
Atlanta	564	149	Las Vegas	1038	274	Virginia:	420	111
Hawaii:	746	197	New Hampshire	435	128	Richmond	644	170
Honolulu	780	206	New Jersey:	526	139	Washington:	1200	317
Idaho	897	237	Elizabeth	314	83	Seattle	1091	288
Illinois:	772	204	New Mexico:	772	204	West Virginia:	568	150
Chicago	871	230	Albuquerque	746	197	Morgantown	549	145
Indiana:	534	141	New York:	609	161	Wisconsin:	587	155
Indianapolis	508	134	New York City	1046	276	Milwaukee	659	174
Iowa:	466	123	Rochester	663	175	Wyoming:	746	197
Des Moines	534	141	North Carolina:	644	170	Chenne	841	222
Kansas:	587	155	Greensboro	492	130	District of Columbia	799	211
Wichita	508	134	North Dakota:	477	126	Puerto Rico	326	86
Kentucky:	314	83	Fargo	515	136	United States*	628	166
Louisville	655	173	Ohio:	594	157			
Louisiana:	545	144	Akron	492	130			
Shreveport	519	137						

Note: L x 0.2642 = gal.

Source: Metcalf and Eddy, 1979.

TABLE III-46

TYPICAL MUNICIPAL WASTE CONCENTRATIONS

Constituent	Concentration mg/l Strong	Concentration mg/l Medium**	Concentration mg/l Weak
Solids, total	1,200	720	350
Dissolved, total	850	500	250
Fixed	525	300	145
Volatile	325	200	105
Suspended, total	350	220	100
Fixed	75	55	20
Volatile	275	165	80
Settlable solids, (ml/liter)	20	10	5
Biochemical oxygen demand, 5-day, 20^0 (BOD_5-20^0)	400	220	110
Total organic carbon (TOC)	290	160	80
Chemical oxygen demand (COD)	1,000	500	250
Nitrogen, (total as N)	85	40	20
Organic	35	15	8
Free ammonia	50	25	12
Nitrites	0	0	0
Nitrates	0	0	0
Phosphorus (total as P)	15	8	4
Organic	5	3	1
Inorganic	10	5	3
Chlorides*	100	50	30
Alkalinity (as $CaCO_3$)*	200	100	50
Grease	150	100	50

*Values should be increased by amount in carriage water.
**In the absence of other data use medium strength data for planning purposes.

Source: Metcalf and Eddy, 1979

TABLE III-47

MUNICIPAL WASTEWATER TREATMENT SYSTEM PERFORMANCE

Influent: "Raw-Medium Strength Domestic Sewage" see Scheme Number 0 for characteristics.

Scheme Number**	Effluent Concentrations (mg/l), (% Total Removal Efficiencies*)				
	BOD_5	COD	SS	P_T, (mgP/l)	N_T, (mgN/l)
0 Raw waste water	200 (0%)	500 (0%)	200 (0%)	10 (0%)	40 (0%)
1	130 (35%)	375 (25%)	100 (25%)	9 (10%)	32 (20%)
2	40 (80%)	125 (75%)	30 (85%)	7.5 (25%)	26 (35%)
3	25 (88%)	100 (80%)	12 (94%)	7 (30%)	24 (40%)
4	18 (91%)	70 (86%)	7 (96%)	1 (90%)	22 (45%)
5	18 (91%)	70 (86%)	7 (96%)	1 (90%)	4 (90%)
6	13 (94%)	60 (88%)	1 (99.5%)	1 (90%)	3 (92%)
7	2 (99%)	15 (97%)	1 (99.5%)	1 (90%)	2 (95%)

* Efficiencies for wastewater treatment are for the approximate concentration range, as measured by BOD_5, of $100 \le BOD_5 \le 400$, (mg/l).

**

Scheme No.	Process
0	No treatment.
1	Primary
2	Primary, plus Activated Sludge (Secondary Treatment)
3	Primary, Activated Sludge, plus Polishing Filter (High Efficiency or Super Secondary)
4	Primary, Activated Sludge, Polishing Filter, plus Phosphorus Removal and Recarbonation
5	Primary, Activated Sludge, Polishing Filter, Phosphorus Removal, plus Nitrogen Stripping and Recarbonation
6	Primary, Activated Sludge, Polishing Filter, Phosphorus Removal, Nitrogen Stripping Recarbonation, plus Pressure Filtration
7	Primary, Activated Sludge, Polishing Filter, Phosphorus Removal, Nitrogen Stripping Recarbonation, Pressure Filtration, plus Activated Carbon Adsorption

Source: Meta Systems, 1973

TABLE III-48

POINT SOURCE LOADINGS OF SIX MAJOR WASTEWATER TREATMENT FACILITIES IN ONE NORTH CAROLINA 208 AREA

FACILITY NAME	FLOW (MGD)	BOD (lb/day)		S.S. (lb/day)		Sludge Production
		INFLUENT	EFFLUENT	INFLUENT	EFFLUENT	(lb/day Dry Solids)
Northside	8.4	16,673	1,331	13,731	2,522	4,300
Third Fork	3.4	7,231	993	5,189	2,410	3,300
New Hope	3.4	5,473	1,758	4,197	1,361	318
Chapel Hill	3.8	5,166	824	5,071	1,363	3,000
Walnut Creek	20.3	64,673	11,005	23,702	7,111	6,255
Hillsborough	0.56	957	383	934	234	
SUB-TOTAL	39.9	100,173	16,294	52,824	15,001	17,173

Because of the difficulty in characterizing industrial wastes in general, the user is advised to get as much data as possible locally. Water use (flow rate) as well as variety in unit processes will have a profound effect on pollutant loads. If local data is unavailable, the best sources of information on industrial waste characterization is the "Effluent Guidelines" series of reports by the U.S. EPA. A report is available for each of the EPA point source categories. These reports contain typical waste characteristics for various processes within the point source category as well as process water usage and are listed in the references at the end of the chapter. Effluent limitations are also given which can be used as upper bound concentrations in water quality assessments.

In addition to process variation, industries also employ various types of waste reduction measures in the plant and in plant wash treatment facilities. In-plant measures include

- recirculation of non-contaminated water
- segregation of contaminated and non-contaminated waters prior to treatment
- removal of semidry residues and
- flow reduction

Eckenfelder (1970) presents information on industrial waste concentrations and loads, waste reduction measures and industrial waste treatment.

Table III-49 contains some typical pollutant loads which might result from the industries shown. Table III-50 also presents loads for some industries and typical removal efficiencies and expected loads. These waste water treatment processes are representative though not exhaustive of techniques which may be used. Values in Tables III-49 and III-50 are for comparison only. They should not be used for load projecting in other areas.

TABLE III-49

TYPICAL INDUSTRIAL DISCHARGE POLLUTANT CONCENTRATIONS

Industry	Flow Rates mg/1000 lb[1]	BOD lb/1000 lb	COD lb/1000 lb	TSS lb/1000 lb	Total N lb/1000 lb	Total P lb/1000 lb	Heavy Metal lb/1000 lb	Oil & Grease lb/1000 lb
Primary Metal[2]	0.2-1.6	-	-	-	32	15	55-242	-
Cu, Brass Rods[3]	0.04	0.1	0.5	0.02	0.07	~0	-	-
Roofing Materials[3]	0.01	13.6	25.7	14.2	0.34	~0	0.13	0.68
Steel Plate, Wire[3]	0.004	0.56	2.7	5.1	0.04	0.01	1.2	0.12
Petroleum (General)[2]	0.005	1.3	3.7	-	0.4	-	0.003	0.15
Oil Production(#1)[3]	0.003	0.57	2.1	0.58	0.33	0.01	0.05	0.14
Oil Production(#2)[3]	0.003	0.45	1.3	0.86	0.16	0.01	0.03	0.09
Oil Production(#3)[3]	0.001	0.45	2.9	0.65	0.24	0.01	0.04	0.31
Paper (General)[2]	0.015	18	55	28	-	-	-	-
Paperboard[3]	0.017	19.6	64.8	37.9	0.05	-	-	-
Paper[3]	0.024	12.6	43	33.1	0.03	-	-	-
Primary Inorganic[2]	0.002	0.2-3.5	-	5-30	0.03-0.7	0.8-9.0	0.05-0.3	0.06-2
Alky Lead Fluoro Hydrocarbons[3]	0.002	0.39	0.89	0.15	0.03	-	-	0.1
Inorg. Acids[3]	0.004	0.08	0.52	5.37	0.04	0.02	0.33	0.06
Primary Organic[2]	0.002	1-1.9	-	-	3-7	0.15-0.3	0.01-0.02	0.05-0.08
Caustic Chemicals[3]	0.021	1.24	4.9	19.9	1.27	0.3	1.69	0.24
Plant Food[3]	0.001	0.03	1.43	0.01	1.17	0.14	0.02	0.02

[1] Units are million gallons of pollutant per 1000 lb. of finished product

[2] Kaiser Engineers, 1969

[3] Pearson, Storrs, Sellech, 1969

TABLE III-50

SUMMARY OF CURRENT AND PROJECTED WASTE LOADS IN ONE REGION 208 AREA (BY SIC CODE)

SIC GROUP		CURRENT LOADINGS		BEST PRACTICABLE WASTE REDUCTION TECHNOLOGY			PROJECTED LOADINGS	
		BOD (lb/day)	SS (lb/day)		Expected Reductions		BOD (lb/day)	SS (lb/day)
No.	Description	Sewer	Sewer	Description	BOD(%)	SS(%)	Sewer	Sewer
201	Meat Products	1,523	1,059	Anaerobic Lagoon to Stabilization Pond	90	85	152	117
202	Dairy Products	973	400	Anaerobic Digestion & Clarification	85	90	71	40
204	Grain Mill Prods.	180	50	Oxidation Ditch & Clarification	85	75	27	13
205	Bakery Prods.	935	910	Rotating Bio-Filters & Clarification	85	65	140	319
208	Soft Drinks	330	40	Fixed Activated Sludge	84	65	53	14
211	Tobacco Man.	2,024	1,750	Activated Sludge (E.A.) & Clarification	85	75	304	438
22_	Textile Mill	2,530	2,173	Activated Sludge & Alum-Aided Clarif.	85	75	380	543
226	Dyeing & Fin.	0	0	Carbon Adsorption & Clarification	75	60		
251	Furniture	0	0	--	--	--		
265	Paperboard Con.	245	150	Screening, Ext. Aeration, Clarification	35	65	159	53
27_	Print. & Pub.	0	0	--	--	--		
28_	Chem. & Allied P.	64	29	Activated Sludge & Clarification	85	75	10	18
32_	Stone, Clay P.	0	0	Stilling Ponds, Water Recycle	30	70		
35_	Machinery.	32	79	Oil & Grease Traps	50	65	16	28
36_	Elect. Equip.	659	402	Ion Exchange (for Plating Process)	10	90	593	40
379	Transp. Equip.	100	100	Oil & Grease Traps	50	65	50	50
---	Non-Manuf.	1,374	170	See Text	70	90	412	17
9999	Mun. W.W.T.P.	0	0	Upgrade Six Largest Plants	Varies for Each Plant			
	TOTALS	10,469	7,312	--	--		2,367	1,690

3.4.4 Priority Pollutants in Municipal and Industrial Waste Waters

The priority pollutants which appear in municipal wastewaters comes from three main sources

- industrial effluents
- nonpoint source runoff and
- domestic uses

The proportion from each category will vary from location to location as well. The types of pollutants in Table III-51 are those occurring most frequently in household wastewaters.

According to the data of Feiler (1980) of the 129 priority substances only 27 occurred at least 30 percent of the time in his sampled treatment plant influents (Table III-52). Of those 27, eight were metals. Of the five most frequently detected, three were metals (zinc, copper and chromium). The loading of metals in the influent is substantially affected by the percentage of industrial effluent as shown in Figure III-18. The slope of the regression line is 72.86 μg/l/percent.

The mixture of priority substances found in municipal influent will depend primarily on the mixture of industries contributing flow. Table III-53 contains 42 of the 129 priority pollutants categorized by the industrial effluents in which they will likely be found. This table is based on screening data provided by U.S. EPA (Neptune, 1981). The 42 which appear are those which most frequently appeared in the screening data. The intent of the table is not to imply that these chemicals are necessarily the most problematic (i.e. carcinogenic, toxic) but only that they are the most ubiquitous. Characterization of influent concentrations for these pollutants is not currently possible. Maximum and minimum values such as those shown in Table III-52 are more typical of the available data. If data for a particular priority pollutant is necessary some sampling of the influent and effluent of the treatment plant is recommended.

TABLE III- 51

PREDICTED PRIORITY POLLUTANTS IN HOUSEHOLD WASTEWATER

Organics	Inorganics
benzene	arsenic
phenol	cadmium
2,4,6-trichlorophenol	chromium
2-chlorophenol	copper
1,2-dichlorobenzene	lead
1,4-dichlorobenzene	mercury
1,1,1-trichloroethane	zinc
naphthalene	antimony
toluene	silver
diethylphthalate	
dimethylphthalate	
trichloroethylene	
aldrin	
dieldrin	

Source: Hathaway, 1980

TABLE III- 52[a]

OCCURRENCE OF PRIORITY POLLUTANTS IN POTW INFLUENT SAMPLES

Parameter	Number of Samples Analyzed	Percent of Times Detected	Minimum[c]	Maximum[c]
Zinc	146	100	23	7680
Copper	146	100	34	1190
Cyanide	150	99	3	2500
Chromium	146	99	8	2380
Toluene	152	98	2	500
Tetrachloroethylene	152	97	2	1100
Chloroform	152	96	1	430
Methylene Chloride	152	95	1	11000
Trichloroethylene	152	95	1	860
Bis(2-ethylhexyl) phthalate	152	94	2	390
1,1,1-Trichloroethane	152	91	1	1600
Nickel	146	87	11	1930
Ethylbenzene	152	86	1	448
Silver	146	84	2	77
Phenol	152	83	1	380
Lead	146	79	16	935
Cadmium	146	71	1	1800
Mercury	146	70	200	3900
Benzene	152	68	1	1560
Di-n-butyl phthalate	152	63	1	105
Diethyl phthalate	152	62	1	33
Butyl benzyl phthalate	152	59	2	140
1,2-Trans-dichloroethylene	152	58	1	97
Naphthalene	152	55	1	150
1,1-dichloroethane	152	40	1	24
1,1-dichloroethylene	152	35	1	243
1,2-dichlorobenzene	152	30	2	440

[a] Only those substances detached at least 30% of the time are included.
[b] Source: Feiler, 1980
[c] Units of μg/l

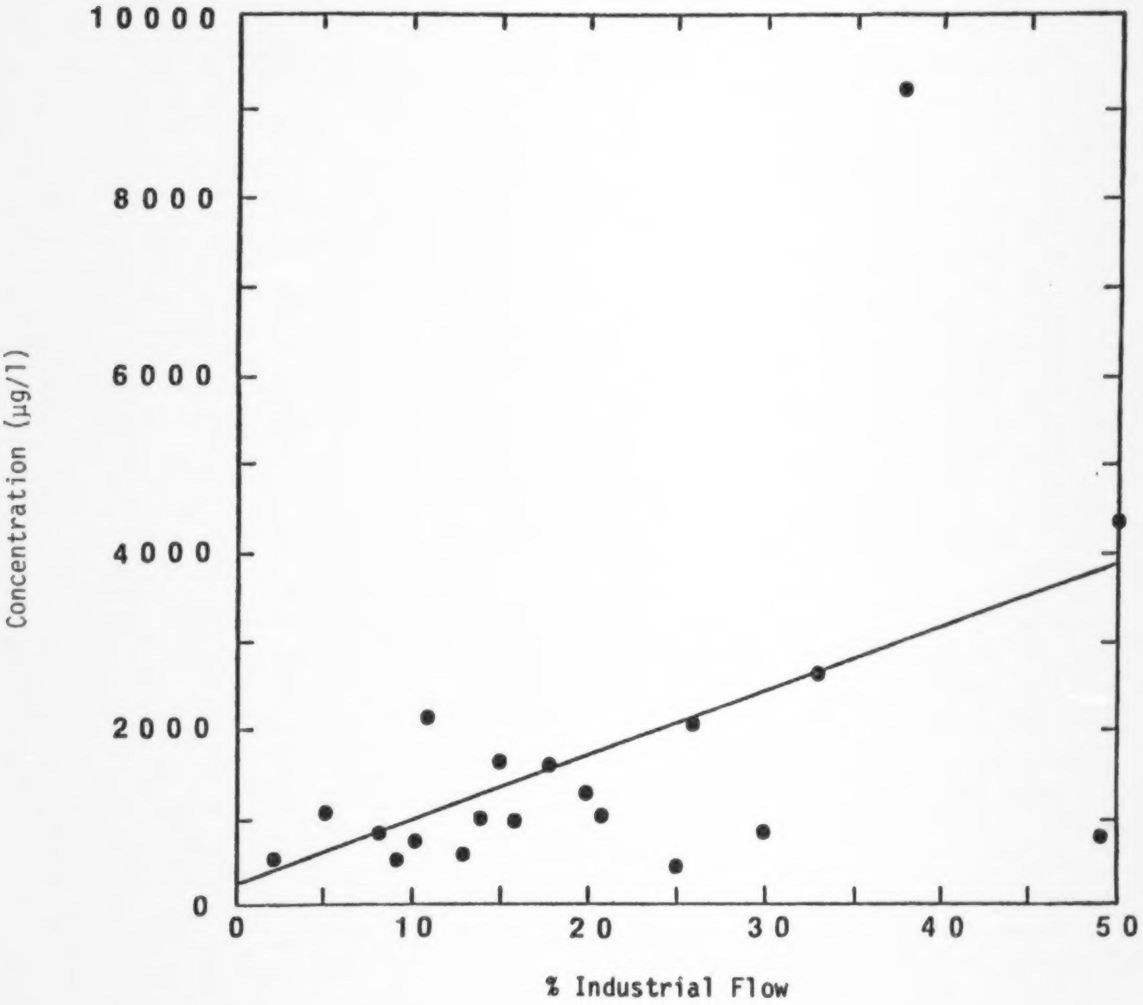

FIGURE III-18 CORRELATION OF INFLUENT TOTAL METALS CONCENTRATION TO PERCENT INDUSTRIAL FLOW

Source: Feiler, 1980

TABLE III-53

INDUSTRIAL CATEGORIES AND FREQUENTLY DETECTED PRIORITY POLLUTANTS BY CATEGORY

	Soaps & Detergents	Adhesives & Sealants	Leather	Textiles	Gum & Wood	Pulp & Paper	Timber	Printing & Publishing	Paint & Ink	Pesticides	Pharmaceuticals	Organics & Plastics	Rubber	Coal Mining	Ore Mining	Paving & Roofing	Steam & Electric	Petroleum Refining	Iron & Steel	Foundries	Electroplating	Nonferrous Metals	Batteries	Coil Coating	Photographic	Inorganic Chemicals	Electrical	Auto & Other Laundries	Phosphates	Plastics Processing	Explosives	Porcelain/Enameling	Landfill	Mech. Products	POTWs	Oil & Gas
Benzene							●		●			●		●					●																	
Carbon tetrachloride												●																								
Chlorobenzene												●																								
1,2 dichloroethane												●																								
1,1,1 trichloroethane												●																						●		
Chloroform								●	●			●		●					●			●													●	
1,1 dichlosoethylene												●																								
1,2 trans-dichlosoethylene												●																								
2,4 dimethylphenol												●																								
Ethylbenzene												●																								
Methylene chloride							●	●	●		●	●		●			●					●					●							●	●	
Dichlorobromonethane												●																								
Trichlorofluoromethane												●																								
Naphthalene												●							●																	
Pentachlorophenol							●																													
Phenol				●			●					●							●															●	●	
Bis(2-ethylhexyl) phthalate				●								●		●					●	●		●													●	
Butyl benzyl phthalate												●							●																	
Di-n-butyl phthalate												●							●																	
Di-n-octyl phthalate																			●																	
Dimethylphthalate												●																								
Chrysene																			●																	
Anthracene												●							●																	
Flourene																			●																	
Phenanthrene												●																								
Pyrene																			●																	
Tetrachloroethylene												●																						●		
Toluene				●			●	●				●		●					●														●	●		
Trichloroethylene												●																								
Antimony				●								●							●			●														
Arsenic												●										●														
Beryllium																			●																	
Cadmium								●	●			●							●		●															
Chromium				●	●			●	●				●						●							●										
Copper			●	●				●	●			●			●				●	●																
Cyanide				●				●				●																								
Lead			●	●				●				●																								
Mercury												●																								
Nickel				●																																
Silver				●				●																												
Thallium												●																								
Zinc			●	●											●					●						●										

Source: Neptune, 1980

The evaluation of priority pollutant loads in municipal wastes is the same as for conventional parameters. First, the influent concentration is estimated and then the removal of the substance is estimated. Data such as that found in Table III-54 can be used to estimate the removal efficiency for some compounds.

The data of Table III-55 give typical concentrations of some priority pollutants in municipal primary and secondary effluent.

EXAMPLE III-8

Estimation of Municipal Waste Treatment Loads of Trichloroethylene

A municipal waste treatment plant has a mean influent concentration of 40 μg/l of trichloroethylene. The plant employs a trickling filter for secondary treatment. Estimate the daily trichloroethylene effluent load. The plant flow rate is 1 mgd.

Solution:

From Table III-54 the removal efficiency of trickling filters for trichloroethylene (TCE) is 96 percent.

Equation III-64 gives the effluent load. Since the plant flow rate is known the estimate of flow $(Q_p \cdot P_p)$ is not necessary. The flow rate of 1 mgd (3.8×10^6 l/day) can be substituted for $(Q_p \cdot P_p)$.

$$Y(TCE)_m = 3.8 \times 10^6\ (40)(1-.96) \times 10^{-9}$$

$$= 6 \times 10^{-3} \text{ kg-TCE/day}$$

END OF EXAMPLE III-8

TABLE III-54

REDUCTION OF CONVENTIONAL AND PRIORITY POLLUTANTS BY POTW TREATMENT PROCESSES

Fraction	Parameter	Percent Removal				
		Primary Treatment(1)	Trickling Filter(2)	Activated Sludge(3)	Activated Sludge(4)	Tertiary Treatment(5)
Conventionals	BOD	17	93	95	90	95
	Total Suspended Solids	39	94	94	88	98
	COD	13	62	90	80	91
	Oil and Grease	52	69	89	90	71
Organics	Benzene	23	96	95	99+	99+
	1,1,1 - Trichloroethane	47	92	87	38	99
	Chloroform	23	60	79	11	25
	1,2 - Trans-Dichloroethylene	68	98	57	99+	99+
	Ethylbenzene	25	92	92	80	98
	Methylene Chloride	14	47	77	27	92
	Tetrachloroethylene	-	78	82	-	98
	Toluene	-	87	71	96	99
	Trichloroethylene	30	96	89	44	99
	Phenol	55	96	13	99+	99
	Naphthalene	0	99+	28	99+	-
	Bis (2-Ethylhexyl) Phthalate	-	54	78	40	60
	Butyl Benzyl Phthalate	36	97	48	99+	99+
	Di-N-Butyl Phthlate	99+	0	31	99+	64
	Diethyl Phthlate	11	96	10	99+	99+
Metals	Cadmium	-	74	92	99+	99+
	Chromium	0	74	91	76	87
	Copper	24	89	90	84	88
	Cyanide	57	81	71	53	-
	Lead	-	94	74	99+	97
	Mercury	-	99+	54	86	86
	Nickel	-	25	60	18	51
	Silver	17	95	83	99+	99+
	Zinc	27	80	86	83	87

(1) Two Plant data base
(2) Three Plant data base
(3) Seventeen plant data base
(4) One plant data base
(5) Three plant data base

TABLE III-55

CONCENTRATIONS (MEAN ± STANDARD ERROR) OF EPA PRIORITY POLLUTANTS IN THE LOS ANGELES COUNTY JWPCP EFFLUENTS[a]

	Primary	Secondary
Flow (liters/yr x 10^{11})	4.71	0.007
pH	7.3	7.3
General constituents (mg/liter)		
Total suspended solids	131	18
Oil and grease	34	1.6
Ammonia nitrogen	37	30
Nitrate nitrogen	NA	NA
Total (K) nitorgen	49	NA
Total phosphorus	20	NA
BOD	200	9.0
COD	460	83
Fecal coliform (MPN/100 ml)	7.5 x 10^6	7.5 x 10^4
Volatile organics (µg/liter)		
Benzene	200 ± 34	22 ± 2
Carbon tetrachloride	12 ± 2	16 ± 0
Chlorobenzene	12 ± 7	3
1,2-dichloroethane	<10	11 ± 1
1,1,1-trichloroethane	130 ± 15	180 ± 15
Chloroform	34 ± 0	30 ± 2
Ethylbenzene	130 ± 6	18 ± 4
Methylene chloride	24 ± 2	4 ± 0
Dichlordifluoromethane	6	<10
Dichlorobromomethane	<10	6
Tetrachloroethylene	54 ± 14	160 ± 25
Toluene	310 ± 24	24 ± 4
Trichloroethylene	140 ± 5	12 ± 2
Extractable organics (µg/liter)		
Acenaphthene	<10	<10
1,2-dichlorobenzene	<10	<10
1,4-dichlorobenzene	<10	<10
2,4-dimethylphenol	14 ± 2	<10
Bis (2-chloroethoxy) methane	<10	<10
Naphthalene	<10	<10
Nitrobenzene	<10	<10
N-nitrosodiphenylamine	11 ± 6	<10
Phenol	180 ± 160	14 ± 8
Pentachlorophenol	40 ± 35	<10
Bis (2-ethylhexyl) phthalate	16 ± 10	4 ± 1
Di-n-butyl phthalate	42 ± 2	90 ± 47
Diethyl phthalate	<10	<10
Dimethyl phthalate	20 ± 14	<10
Miscellaneous		
Asbestos (10^6/liter)	NA	NA
Cyanide (µg/liter)	NA	NA
Phenol (mg/liter)	NA	NA
Trace metals (mg/liter)		
Antimony	0.008	0.003
Arsenic	0.004	0.004
Beryllium	0.0001	0.0002
Cadmium	0.018	0.008
Chromium	0.22	0.090
Copper	0.14	0.050
Mercury	0.0003	0.0001
Manganese	0.07	0.043
Nickel	0.20	0.22
Lead	0.11	0.003
Selenium	0.007	0.007
Silver	0.005	0.002
Thallium	<0.0001	0.001
Zinc	0.37	0.26

[a] NA means "not analyzed".

Source: Young, 1979

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CHAPTER 4

RIVERS AND STREAMS

4.1 INTRODUCTION

The purpose of this chapter is to present simplified tools which can be used to predict responses of rivers and streams to the impact of pollutants. The introductory sections to the chapter should be read prior to solving any problems in order to become familiar with the topics that will be covered and the limitations of the formulations presented.

Rivers throughout this country are subject to a wide spectrum of geological, biological, climatological, and anthropogenic impacts which produce a variety of water quality problems. Approaches which provide guidance to the solution of these problems, especially ones restricted to hand calculations, must be limited in scope. The following guidelines have been used in selecting topics to be considered in this chapter: 1. widely occuring problems, 2. those amenable to hand calculations, and 3. those for which planners can obtain sufficient data.

4.1.1 Scope

The major problem areas to be considered are:

- Carbonaceous (CBOD) and Nitrogenous (NBOD) Biochemical Oxygen Demand
- Dissolved Oxygen
- Temperature (with a discussion of low flow)
- Nutrients and Eutrophication Potential
- Coliform Organisms
- Conservative Constituents
- Sedimentation and Suspended Solids
- Toxic Substances

Beginning in 1974, the U.S. Environmental Protection Agency has for several years published the National Water Quality Inventory which is a compilation of current water quality conditions and recent trends in the nation's rivers and lakes. Several of the tables in that report series are relevant to this document and are included here. Table IV-1 illustrates reference water quality levels used to define acceptable pollutant limits in U.S. waterways. Table IV-2 shows water quality conditions in eight major waterways in the United States, while Table IV-3 summarizes the most widely observed water quality problems in the U.S. These tables will be cited throughout this chapter.

Local water quality standards, when they exist, are preferable to the general guidelines provided in Table IV-1. Table IV-4 shows example standards for dissolved oxygen and water temperature for the states of Virginia and Maryland. Parts of the standards are significantly different from the reference levels in Table IV-1. For example the daily average dissolved oxygen standard for natural trout water for the state of Virginia is 7.0 mg/l, while 5.0 mg/l is recommended for the protection of aquatic life (Table IV-1). Thus, when local standards exist, they should be used in lieu of general reference levels.

4.1.2 Significance of Problem Areas

Oxygen depletion is often the result of excessive CBOD and NBOD loadings particularly in combination with high temperature and low flow conditions. Increased nutrient loadings to streams which produce elevated ambient concentrations can pose substantial potential for eutrophication. The nutrient problem is currently one of the most widespread areas of concern regarding river water quality. The health hazards category in Table IV-3 lists elevated coliform levels as a problem of particular concern in northeastern and Great Lakes States. Salinity has been identified as a major problem in the central and southwestern states.

TABLE IV-1

REFERENCE LEVEL VALUES OF SELECTED WATER QUALITY INDICATORS FOR U.S. WATERWAYS (U.S. EPA, 1976)

Parameter	Reference Level
Ammonia	$\leq$ 0.02 mg/l as unionized ammonia (for freshwater aquatic life)
Color	$\leq$ 75 platinum-cobalt units (for water supply)
Dissolved Oxygen	$\geq$ 5.0 mg/l (to maintain fish populations)
Dissolved Solids	$\leq$ 250 mg/l (for water supply)
Fecal Coliforms	log mean $\leq$ 200 per ml over 30 days and 90 percent $\leq$ 400 per ml (for bathing waters)
Nitrate-N	$\leq$ 10 mg/l (water supply)
pH	between 6.5 and 9.0 (for freshwater aquatic life)
Phenols	$\leq$ 1 μg/l (for water supply)
Suspended Solids and Turbidity	shall not reduce the depth of the compensation point by more than 10 percent (aquatic life)
Total Dissolved Gases	$\leq$ 110 percent saturation (aquatic life)

TABLE IV-2

CONDITION OF EIGHT MAJOR WATERWAYS (EPA,1974)

River	Harmful Substances	Physical Modification	Eutrophication Potential
Mississippi		High* turbidity and solids below Missouri River	High*, increasing nutrients but no algae
Missouri	Trace metals present in middle river	High* suspended solids, turbidity in middle and lower river	High*, increasing nutrients but no algae
Ohio	High*, increasing iron and manganese	High* suspended solids in lower river, some improvements	High* nutrients but no algae
Tennessee			Small increase in nutrients but no algae
Detroit area rivers	Cyanide present but dimishing	Suspended solids improving, local temperature effects from discharges	Nutrients discharged to Lake Erie decreasing
Columbia	Severe gas super saturation; some radioactivity in lower river	Occasional high* temperatures	High* nutrients but no algae, except for slime growths in lower river
Snake	Severe gas supersaturation, significant pesticides	Turbidity from natural erosion, agricultural practices, reservoir flushing	Nuisance algal blooms each summer

TABLE IV-2 (continued)

River	Harmful Substances	Physical Modification	Eutrophication Potential
Willamette	Significant sulfite waste liquor from pulp and paper wastes	High* turbidity at high flow, high temperature in summer	High* level of nutrients but not excessive algae

River	Salinity, Acidity, and Alkalinity	Oxygen Depletion	Health Hazards and Aesthetic Degradation
Mississippi	High* salinity, acidity below major tributaries	Oxygen-demanding loads from large cities evident	Commercial fishing eliminated in lower river by phenols, bacteria near cities
Missouri	High* dissolved salts in middle and lower river	High* organic loads from feedlots, improved near cities	High* bacteria and viruses present in wet and dry periods
Ohio	Low* alkalinity especially in upper river	Occasional low* dissolved oxygen near Cincinnati and Pittsburgh	High* bacteria especially in high population areas
Tennessee		Low* BOD and decreasing COD in reservoirs	High* bacteria in small areas near cities, low radionuclides
Detroit area rivers	Acids and chloride low,* improving despite large discharges	Low* dissolved oxygen only at mouths of area tributaries	Phenols decreasing, bacteria unchanged-to-higher

TABLE IV-2 (continued)

River	Salinity, Acidity, and Alkalinity	Oxygen Depletion	Health Hazards and Aesthetic Degradation
Columbia	Approaches ideal for fresh waters	Dissolved oxygen close to saturation	Very low* bacteria
Snake	High* dissolved solids from irrigation in middle river	Dissolved oxygen close to saturation	High* bacteria below population centers
Willamette	Low* dissolved mineral salts, improved pH	Improved dissolved oxygen, no standards violations	High* bacteria, but improving

*High (or low) relative to other rivers, or relative to other sections of river, or to national reference levels. Does not necessarily imply standards violations or dangerous condition.

TABLE IV-3

WATER QUALITY PROBLEM AREAS REPORTED BY STATES*
NUMBER REPORTING PROBLEMS/TOTAL (EPA,1975)

	Middle Atlantic, Northeast	South	Great Lakes	Central	Southwest	West	Islands	Total
Oxygen depletion	11/13	9/9	6/6	6/8	4/4	6/6	4/6	46/52
Eutrophication potential	11/13	6/9	6/6	8/8	2/4	6/6	4/6	43/52
Health hazards	11/13	8/9	5/6	8/8	3/4	5/6	5/6	45/52
Salinity, acidity, alkalinity	3/13	6/9	2/6	6/8	4/4	4/6	2/6	27/52
Physical modification	7/13	3/9	3/6	8/8	3/4	6/6	5/6	35/52
Harmful substances	6/13	6/9	5/6	4/8	4/4	2/6	3/6	30/52

* Localized or statewide problems discussed by the States in their reports.

TABLE IV-4

EXAMPLE RIVER WATER QUALITY STANDARDS

VIRGINIA

Class	Description	Dissolved Oxygen		Temperature, °F	
		Minimum	Average	ΔT_N	T_{MAX}
III	Coastal and Piedmont	4.0	5.0	5	90
IV	Mountainous	4.0	5.0	5	87
V	Put and Take Trout Waters	5.0	6.0	5	70
VI	Natural Trout Waters	6.0	7.0	5	68

MARYLAND

Class	Description	Dissolved Oxygen*		Temperature
		Minimum	Average	Maximum, °F**
I	Water Contact, Recreation	4.0	5.0	90
III	Natural Trout Waters	5.0	6.0	68
IV	Recreational Trout Waters	4.0	5.0	75

*These values apply except where lower values occur naturally.

**These apply outside the mixing zone. If natural temperature of receiving water is greater than the standard, then that becomes the standard.

Because of their importance, each of the problem areas described will be addressed in this chapter. As shown in Table IV-5, many states routinely measure the parameters associated with these problems. The total number of states responding to the survey was 47. Because of the routine surveys conducted, data are commonly available for performing hand calculations. NBOD, though not directly measured, can be found from measurements of organic and ammonia nitrogen. Chloride concentration measurements can be directly converted to salinity.

4.1.3 Applicability to Other Problems

The tools which are presented in this chapter are designed to address specific water quality problems. However, a number of the tools, which are based on the law of mass conservation, can be directly applied to other problems with little or no modification. In the case of temperature prediction, an energy balance is used (which is analogous to a mass balance).

The degree of commonality of source and sinks of a particular pollutant e.g. a nutrient) or water quality indicator (e.g. dissolved oxygen) is responsible for the similarities and differences among the specific equations. For example, CBOD and NBOD produce a similar general effect (oxygen depletion), generally have similar sources and sinks, and for purposes of this study, are assumed to follow first order decay kinetics. Coliforms, also assumed to decay by first order kinetics, are handled by the mass-balance approach. Conservative substances are different from BOD and coliforms in that they do not decay. Finally, there are some instances where a more subjective analysis is indicated, and neither a mass nor energy balance is presented.

Once the similarities among water quality parameters are understood, handling two seemingly different problems can often be accomplished in a straightforward and similar fashion. For example, the distribution of toxic substances that are either conservative or follow a first order decay may be evaluated using techniques described for conservative substances and coliforms, respectively.

TABLE IV-5

WATER QUALITY PARAMETERS
COMMONLY MONITORED BY STATES* (EPA,1975)

Parameter	Number of States
Flow	47
Dissolved oxygen	47
Coliform bacteria	45
Nitrogen (any form)	39
Phosphorus (any form)	35
pH	35
BOD/COD/TOC	27
Water temperature	29
Turbidity	26
Solids (any type)	27
Metals (any type)	17
Chlorides	19
Alkalinity	15
Conductivity	16
Color	11
Sulfate	14

*Only parameters listed by at least 10 States and specified as being part of each State's monitoring program are included.

4.1.4 Sources of Pollutants

Pollutant loadings originate from three general sources: point, nonpoint, and natural. Each of these can constitute a major hurdle in meeting the 1983 goals of fishable and swimmable waters. Specifically, point sources (30 states), nonpoint sources (37 states), and natural conditions (21 states) are all major contributors to water quality problems (EPA, 1975).

It is imperative that the capacity to assess impacts of nonpoint sources be a part of the hand calculation methodology for rivers. Table IV-6 illustrates the importance of nonpoint source nutrient loading for selected rivers in Iowa. Up to 96 percent of the annual phosphorus load and up to 99 percent of the total nitrogen load are from nonpoint sources. Admittedly, quantification of nonpoint source loads is often difficult. Nevertheless, simplified nonpoint source terms will be included in some of the mass-balance formulations. The methodology supplied in Chapter III can be used to estimate the nonpoint source loading rates.

4.1.5 Assumptions

In deriving the mass-balance equations, a number of assumptions were made. Users should be aware of each assumption so that the tools are not misapplied. The most important assumptions are:

- The system is at steady-state
- Dispersion is small compared to advection (i.e. plug flow is assumed)
- The river system is vertically and laterally mixed
- When pollutants decay, the rates are first order.

The steady-state assumption means that conditions are not changing with time, but only as a function of distance along the river. The time scale for steady-state generally should be on the order of a week or longer. For

TABLE IV-6

ANNUAL PHOSPHORUS AND NITROGEN LOAD FOR SELECTED IOWA RIVER BASINS (EPA,1975)

ANNUAL PHOSPHORUS LOAD

River	Total (lbs/year)	Point Sources (lbs/year)	Nonpoint Sources (lbs/year)	Percent of Total from Nonpoint Sources
Floyd	720,207	29,807	690,400	95.9
Little Sioux	1,851,632	129,088	1,722,544	93.0
Chariton	879,916	48,203	831,713	94.5
Des Moines	5,621,007	586,015	5,034,992	89.6
Iowa	1,723,975*	103,445*	1,620,530*	94.0
Cedar	5,099,507	1,526,775	3,572,732	70.1

*Orthophosphate

ANNUAL NITROGEN LOAD

River	Total (lbs/year)	Point Sources (lbs/year)	Nonpoint Sources (lbs/year)	Percent of Total from Nonpoint Sources
Floyd	1,705,984	65,171	1,640,813	96.2
Little Sioux	9,609,556	85,308	9,522,248	99.1
Chariton	1,585,427	24,795	1,560,632	98.4
Des Moines	41,334,897	695,235	40,639,662	98.3
Iowa	2,075,830	91,287	1,984,543	95.6
Cedar	6,804,881	1,552,334	5,252,547	77.2

example, the summer low flow period generally represents a steady-state situation. However, storm events, and the dynamic responses of a river to them, must be considered a transient phenomenon.

Dispersion effects can usually be neglected when pollutant input into a river is continuous. Under these conditions the plug flow assumption is reasonable because the net dispersive transport is small. However, when a slug of pollutant is discharged instantaneously, dispersive transport is important since high concentration gradients exist around the centroid of the discharged pollutant.

The fully-mixed assumption presupposes that concentration gradients exist only in the direction of flow (longitudinal direction) and not in either the vertical or lateral direction. The final major assumption is that all decay rates can be approximated by first order kinetics. This means that the decay rate of a substance is proportional to the amount present. First order decay is traditionally used in CBOD computations, and occasionally in nitrogen oxidation. The oxidation of inorganic nitrogen actually proceeds in stages from ammonia-N to nitrite-N to nitrate-N. However, for purposes of this report, the first order decay rate is acceptable for NBOD and coliforms, as well as CBOD. Before applying first order decay to other substances, however, care should be taken to determine the validity of the assumption.

For a few of the analyses which follow, several of the aforementioned assumptions are relaxed. In the discussion of mixing zones, Section 4.1.9, partial mixing is discussed for wide rivers. In the discussion on toxicants, Section 4.9, the spill analysis requires that an unsteady-state situation be analyzed where the effects of dispersion are included.

4.1.6 Data Requirements

Required in the analysis of most water quality problems are one or more types of data. For example, stream velocity (U), volumetric flow rate (Q), and stream temperatures (T) are commonly needed. Decay rates, specific to the particular problem at hand, are also required.

The U.S. Environmental Protection Agency has published a document (Zison et al., 1978) intended to provide water quality modelers with a comprehensive source of information on rate constants and coefficients. The document provides extensive information on both biological and water quality parameters commonly used in surface water modeling. The contents of the document will be useful to the users of this document, who are often faced with limited information on process rates for the water bodies being analyzed.

Stream velocity is the most basic hydraulic parameter needed for the analyses presented in this chapter. Ideally, the appropriate stream velocity is the travel time of neutrally buoyant particles over the reach being investigated divided by the distance traveled. Note that this concept of velocity is different from the velocity determined by:

$$U = \frac{Q}{A} \tag{IV-1}$$

As defined by Equation IV-1, this concept of velocity exists only at the point in the river where the cross-sectional area is A. If the point of measurement is not typical of the reach being investigated, then neither will the velocity be typical. Consequently, should the user predict stream velocity based on cross-sectional area, a location typical of the river reach being investigated should be chosen.

An alternate method of predicting stream velocity, which does not depend on either flowrate Q or cross-sectional area A is Manning's Equation. A complete description of the use of this approach is given in many texts on surface water hydraulics, one of the best being Chow (1959).

According to Manning's Equation stream velocity under uniform flow conditions is expressible as:

$$U = \frac{1.49}{n} S^{1/2} R_H^{2/3} \tag{IV-2}$$

where

n = Manning's n

S = slope, ft/ft

R_H = hydraulic radius, ft

Manning's n is the roughness of the stream bed, and can be predicted as outlined in Chow (1959). Barnes (1967) provides roughness data for 90 streams in the United States, and includes cross-sectional areas and photographs of the streams investigated. The slope can be estimated using topographic maps to predict elevation changes between two locations, and then overlying a string over the stream path to predict distance. The hydraulic radius (which is the ratio of the cross-sectional area to wetted perimeter) can be estimated in terms of depth when the stream width is much greater than the depth. Specifically,

$$R_H = \begin{cases} \text{depth, if channel cross-section is rectangular} \\ \\ \text{2/3 maximum depth, if channel cross-section is parabolic} \end{cases}$$

4.1.7 Selection of Season

It is reasonable to expect that a particular water quality problem may be more severe at one time of the year than another. Table IV-7 shows that pollutant levels can depend on season (summer or winter) and flow rate (high flow or low flow). Dissolved oxygen problems, for example, are clearly associated with summer, low flow conditions. Consequently, for any particular pollution problem, users should strive to perform the analysis under critical conditions. Where planning is performed with consideration of the aggravated situation, and where proper abatement action is taken, it is likely that pollution concentrations will be below problem levels during other times of the year. If a problem in fact exists, then it is under these conditions that it will be most pronounced.

In the following sections, hand calculation methods for each problem area are described with illustrative examples. Table IV-8 provides a summary of the material presented.

TABLE IV-7

MAJOR WATERWAYS: SEASONAL AND FLOW ANALYSIS, 1968-72 (EPA, 1974)

Parameters	Winter, High Flow	Summer, Low Flow	Winter, Low Flow	Summer, High Flow	Dominant Effect
	(number of reaches exceeding reference levels)**				
Suspended solids	9	5	0	4	High flow
Turbidity	13	4	1	7	High flow
Color	11	6	3	4	High flow
Ammonia	14	3	7	1	Cold weather
Nitrite	3	7	5	1	Low flow
Nitrate(as N)	12	4	8	1	Cold weather
Nitrate(as NO_3)	8	3	6	1	Cold weather
Nitrite plus nitrate	2	3	2	1	Inconclusive
Organic nitrogen	3	6	0	3	Warm weather
Total Kjeldahl nitrogen	3	5	0	3	Warm weather
Total phosphorus	10	3	5	2	Cold weather
Total phosphate	8	3	5	1	Cold weather
Dissolved phosphate	6	3	4	0	Cold weather
Dissolved solids(105°C)	4	7	6	3	Low flow
Dissolved solids(180°C)	3	8	6	2	Low flow
Chlorides	4	15	10	0	Low flow
Sulfates	5	13	5	5	Warm weather, low flow
Alkalinity	6	12	10	0	Low flow
ph	15	4	6	4	Cold weather, high flow
Dissolved oxygen	0	19	0	9	Warm weather
BOD_5	11	6	8	1	Cold weather
COD (.025N)	6	5	3	2	Cold weather
Total coliforms(MFD)*	4	10	2	5	Warm weather
Total coliforms(MFI)*	8	6	2	4	High flow, warm weather
Total coliforms(MPN)*	4	2	3	3	Inconclusive
Fecal coliforms(MF)*	6	6	3	4	Inconclusive
Fecal coliforms(MPN)*	4	0	1	0	Cold weather
Phenols	5	0	1	0	Inconclusive
Odor	4	0	0	0	Inconclusive

*Membrane filter delayed, membrane filter immediate, most probable number, membrane filter.

**Reference levels are available in Table IV-1. Thirty reaches were analyzed during each season.

TABLE IV-8

WATER QUALITY ANALYSES FOR RIVER SCREENING METHODOLOGY

Water Quality Constituent	Computational Procedures	Supporting Information Included
Water temperature	- equilibrium temperature - mixing temperature - temperature profile for point sources	- shortwave solar radiation - longwave solar radiation - vapor pressure
Carbonaceous and nitrogenous biochemical oxygen demand	- BOD profiles for point sources - BOD profiles with benthic sources added - BOD profiles with both benthic and nonpoint sources added	- graphs, tables, and equations for decay rates
Dissolved oxygen	- CBOD-NBOD-DO profile for point sources - DO profiles with photosynthetic oxygen production and benthic uptake added - critical dissolved oxygen conditions - waste assimilative capacity	- reaeration rates for shallow and deep streams - saturation dissolved oxygen levels corrected for temperature, altitude, salinity - photosynthetic oxygen production and benthic uptake data - tabulated solutions for critical dissolved oxygen levels
Nutrients	- growth limiting nutrient - nutrient profiles for point sources - nutrient profiles for nonpoint sources	- nitrogen/phosphorus ratios for growth limitation - nonpoint source loading rates by land use type
Coliform organisms	- coliform profiles for point sources - coliform profiles for nonpoint sources	- decay rates
Sediment	- bed load - suspended load - total load	- median bed particle sizes for numerous rivers - critical shear stress - sediment transport propensity factor - approximate bed load/suspended load relationship
Toxicants	- toxicant profiles for point and nonpoint sources - mass flux volatilized, advected, and transformed - spill analysis of low and high density toxicants - time required to desorb toxicant from bedded sediments	- vapor pressure, solubility,octanol-water portion coefficient for priority pollutants - Henry's Law Constants

4.1.8 River Segmentation

Although the tools presented in this chapter are of a simplified nature they can be used to analyze complex river systems (i.e. those which have a number of different point and nonpoint sources of pollution, tributaries and withdrawals). Analysis of these systems is accomplished by dividing the river into segments. The basic tenet which must be followed is simply this: Segments are created so that one of the analytical tools presented in this chapter can be used to predict the pollutant concentration profile within the segment.

Analyses of river systems normally begin at a segment where the boundary conditions are known, and proceed sequentially downstream. Thus the results found for one segment are used as the upstream boundary condition for the next segment. Based on the tools in this chapter, the following rules should be followed when segmenting:

1. Point sources of pollutants enter the river just above the upstream boundary of a segment. Tributaries are treated as point sources.

2. Nonpoint sources enter a river throughout the length of a segment.

3. Pollutant concentrations at the upstream end of segments are obtained by mixing the pollutant concentration in the river with the contribution of the point source at that location (if one exists). The location where mixing occurs is called a mixing zone.

4. Generally constant hydraulic variables (e.g. depth and velocity) are used throughout a segment. If there is a gradual change in the hydraulic variables over distance, an average value can be used. If there is an abrupt change in the variable, such as a velocity change caused by a significant deepening of the channel, then a new segment can be created at this boundary.

5. Decay rates, reaeration rates, and other rate coefficients remain constant within a segment. If rate coefficients are known to change significantly from one location to another in a river, then different segments should be created. This rule is consistent with rule (4), since rate coefficients are often functions of hydraulic variables.

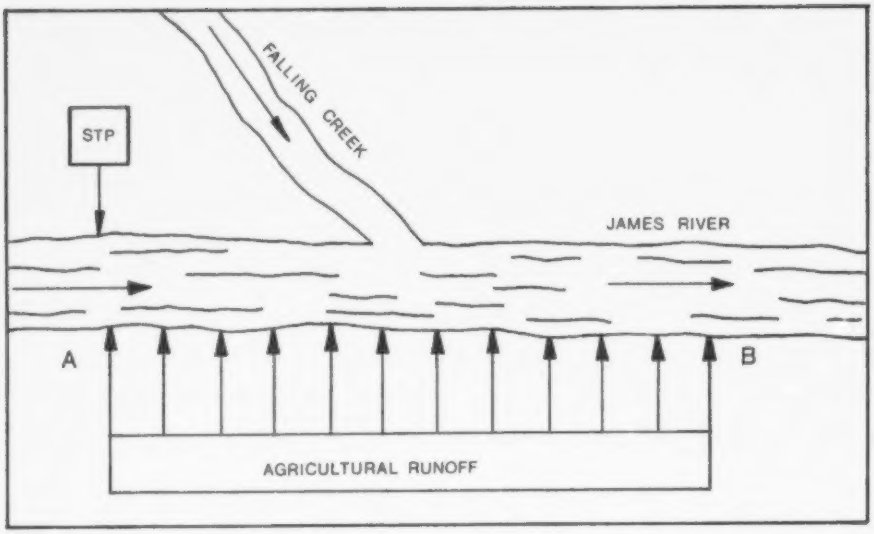
EXAMPLE IV-1

Figure IV-1a shows a stretch of the James River, located in Virginia. On the stretch of the river shown, there is a tributary (Falling Creek), a sewage treatment plant (STP), and a nonpoint source of runoff (agricultural). Segment the river between locations A and B in order to determine the profile of a pollutant which is discharged from each of the three sources.

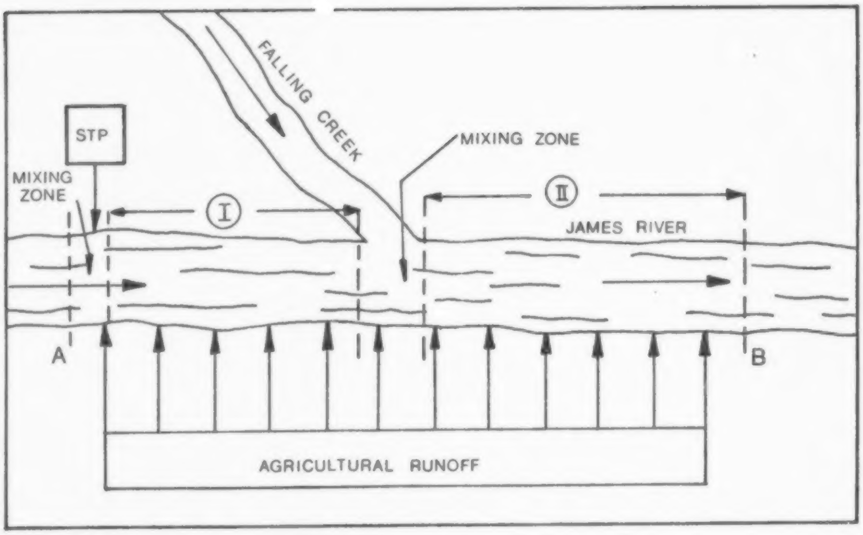
First, it should be noted that often there is more than one way to segment the river to successfully solve the problem. The most obvious method will be illustrated here. Figure IV-1b shows the proposed solution. There are two mixing zones - the first around the treatment plant and the second around the tributary which is treated as a point source. The first segment is located from below the first mixing zone to above the second mixing zone, and has a nonpoint source discharging throughout the length of the segment, consistent with rule (2). The second segment is located below the second mixing zone and continues downstream to location B, which is the end of the nonpoint source. If Falling Creek had not been present, a single segment and a single mixing zone would have been sufficient to analyze the problem.

END OF EXAMPLE IV-1

A second, more comprehensive example will illustrate a number of points about segmentation not covered in the previous example. One of these points is that the segmentation scheme used can vary depending on the pollutant being analyzed.


FALLING CREEK
STP
JAMES RIVER
A
B
AGRICULTURAL RUNOFF

(a) River Segment Being Analyzed


FALLING CREEK
STP
MIXING ZONE
MIXING ZONE
I
II
JAMES RIVER
A
B
AGRICULTURAL RUNOFF

(b) Proposed Segmentation Scheme

FIGURE IV-1 ILLUSTRATION OF RIVER SEGMENTATION PROCEDURE ON THE JAMES RIVER.

EXAMPLE IV-2

Segment the river shown in Figure IV-2 beginning at location A and continuing to location B in order to determine the instream BOD distribution. How would the segmentation differ when predicting the dissolved oxygen profile?

Both point and nonpoint sources discharge to the river in Figure IV-2. Several flows are diverted, and the river width changes over parts of the reach being investigated. Each of the rules stated earlier will be utilized to segment the river system. Figure IV-3 shows one solution to the problem. Depending on the distances between the various sources of pollutants, which are not given in the problem, it might be possible to combine some of the segments. The reservoir is assumed to be analyzed using the methods in Chapter 5, and so is not segmented.

Mixing zones are included around the four point sources: the food processing plant, the tributary, the sewage treatment plant, and the pulp mill. In segments 9 and 11 there appear to be a number of point sources and diversions. Strictly speaking, segments 9 and 11 do not follow the rules presented earlier, which require mixing zones around each point source. However, the point sources and sinks within segments 9 and 11 are assumed to represent equivalent nonpoint sources, which act over the length of each segment. This approach can obviously simplify the analysis of complex river systems by decreasing the number of segments analyzed. However, the analysis is more approximate because the nonpoint source is assumed to be uniformly distributed throughout the segment. Example IV-5 presented later shows a specific application of the concept of an equivalent nonpoint source.

In segment 2 the presence of the small dam is assumed not to influence the BOD profile, so that its presence does not require a mixing zone. However if the dissolved oxygen profile were being calculated, segment 2 would be divided into two segments, with a mixing zone around the dam. This division is required because the dissolved oxygen concentration can rapidly

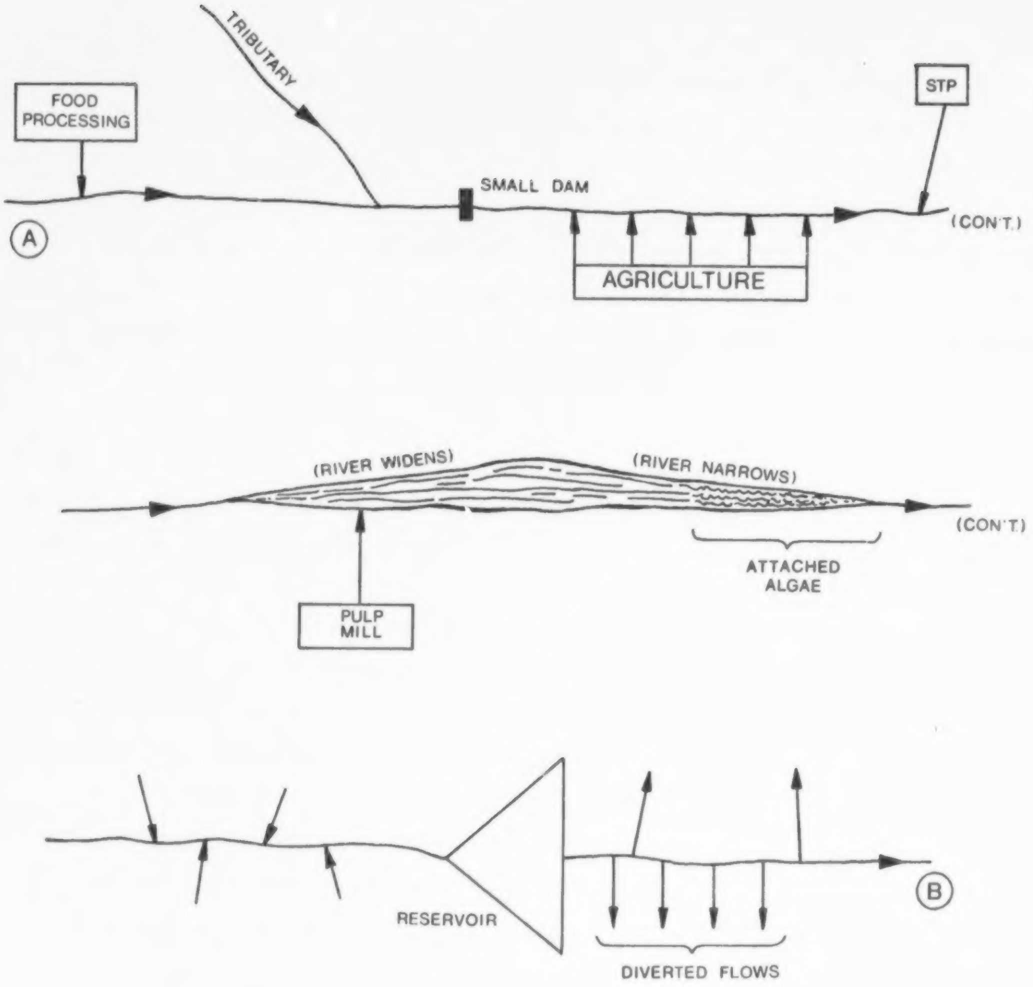
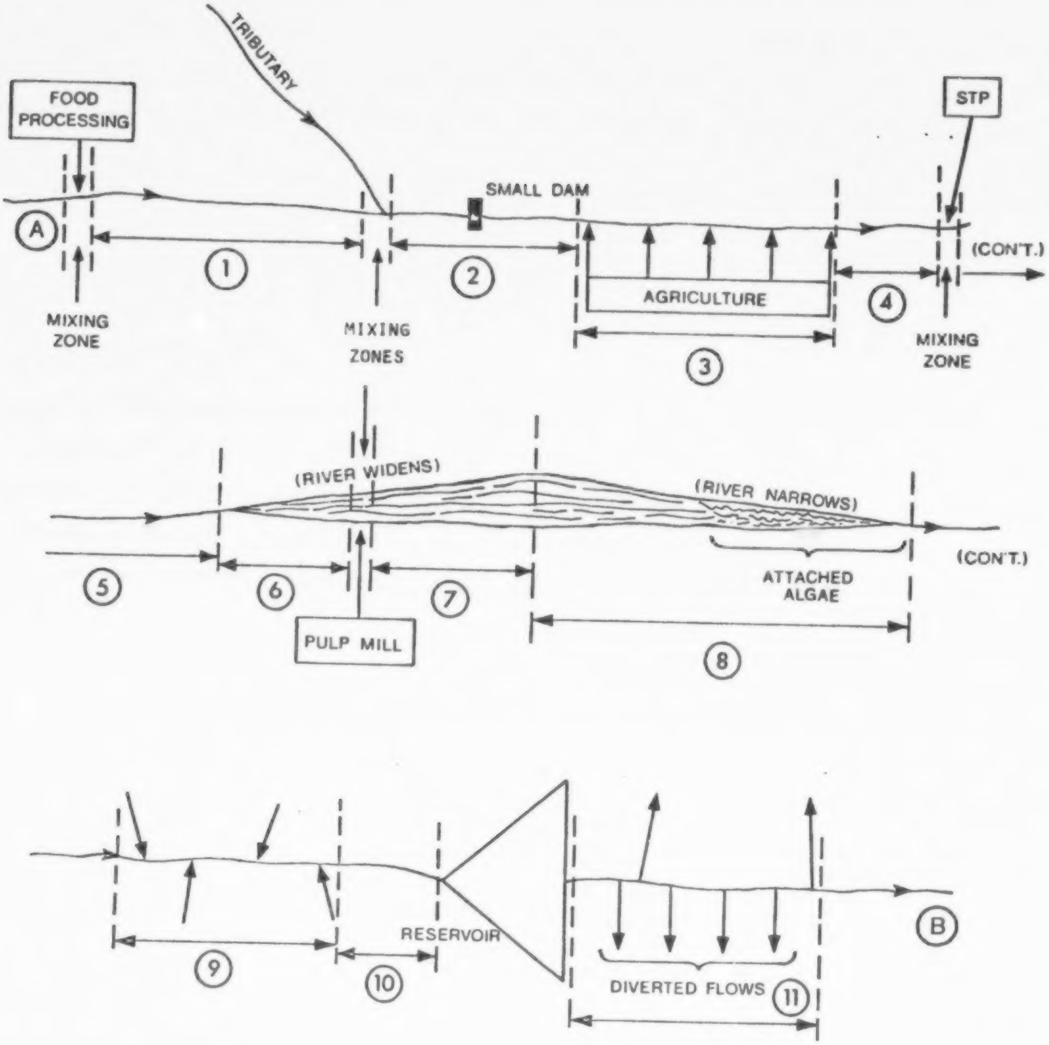

TRIBUTARY
FOOD PROCESSING
STP
SMALL DAM
(CON'T.)
Ⓐ
AGRICULTURE
(RIVER WIDENS)
(RIVER NARROWS)
(CON'T.)
ATTACHED ALGAE
PULP MILL
RESERVOIR
Ⓑ
DIVERTED FLOWS

FIGURE IV-2 HYPOTHETICAL RIVER HAVING A VARIETY OF POLLUTANT SOURCES AND SINKS.



TRIBUTARY
FOOD PROCESSING
STP
SMALL DAM
A
1
2
AGRICULTURE
3
4
(CON'T.)
MIXING ZONE
MIXING ZONES
MIXING ZONE
(RIVER WIDENS)
(RIVER NARROWS)
5
6
7
ATTACHED ALGAE
(CON'T.)
PULP MILL
8
RESERVOIR
9
10
DIVERTED FLOWS
11
B

FIGURE IV-3 RIVER SEGMENTATION FOR BOD DISTRIBUTION.

change (almost instantaneously) as the water flows over the dam. The dissolved oxygen concentration just below the dam should be used as the upstream boundary conditions for the next segment. The specific information required to accomplish this is discussed later in Section 4.3.

A second difference in segmenting for dissolved oxygen occurs in Segment 8. The presence of the attached algae is assumed not to influence the BOD profile, but the algae are internal sources of oxygen. Thus segment 8 would be subdivided at the upstream location of the attached algal growth.

END OF EXAMPLE IV-2

4.1.9 Mixing Zones

A mixing zone, as used in this document, is nothing more than a short reach of a river where a point source and river water mix. It is often assumed, for both simple and more complex approaches (e.g. QUAL-II computer model), that mixing is instantaneous and complete across the entire width of the channel. With several exceptions, such an approach is used in this document.

Assuming complete mixing, the concentration of a pollutant in a river after mixing is:

$$C = \frac{C_u Q_u + C_w Q_w}{Q_w + Q_u} \qquad \text{(IV-3a)}$$

$$= \frac{C_u Q_u + W/5.38}{Q_w + Q_u} \qquad \text{(IV-3b)}$$

where

C = concentration of pollutant in river following mixing, mg/l
C_w = concentration in point source, mg/l
C_u = concentration in river above point source, mg/l
Q_w = discharge rate of point source, ft^3/sec
Q_u = flow rate of river above point of discharge, ft^3/sec
W = pollutant mass emission rate, lbs/day

The concentration C is the pollutant level in the mixing zones shown in the earlier Figures IV-1 and IV-3. These concentrations become the upstream boundary conditions for the adjacent downstream segment.

Although it is convenient to assume that complete mixing occurs, this assumption may be inaccurate for wide rivers, depending on the characteristics of the point source outfall and diffuser. Figure IV-4 illustrates such a case. The river is wide enough so that the wastewater is initially mixed with only a fraction of the total river flow. As the pollutant-riverwater mixture is transported downstream mixing continues until the pollutant is completely mixed across the channel.

The initial pollutant concentration at the point of discharge is

$$C = \frac{\frac{Y}{W} Q_u C_u + Q_w C_w}{Q_w + \frac{Y}{W} Q_u} \qquad \text{(IV-4)}$$

where

$\frac{Y}{W}$ = fractional distance across river where initial mixing occurs.

and all other variables have been previously defined.

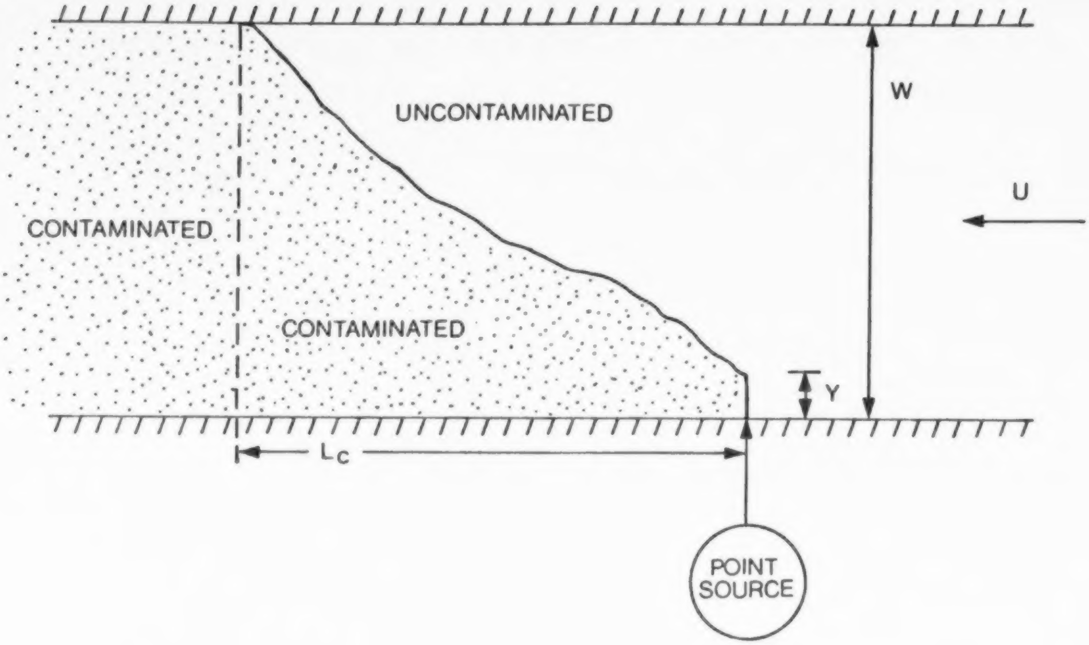
The significance of incomplete initial mixing is that pollutant concentrations can be initially much higher than if complete mixing occurs. For example, if the upstream contribution of the pollutant is negligible ($C_u = 0$) and if the fraction of river flow which initially mixes is far greater than the wastewater flow ($\frac{Y}{W} Q_u >> Q_w$), then

$$C = \frac{W}{Y} C_{cm} \qquad \text{(IV-5)}$$

where

C = concentration of pollutant if there is incomplete initial mixing

C_{cm} = concentration of pollutant if there is complete initial mixing



UNCONTAMINATED
W
U
CONTAMINATED
CONTAMINATED
Y
L_C
POINT SOURCE

FIGURE IV-4 POLLUTANT DISCHARGE WHERE INITIAL MIXING OCCURS A FRACTIONAL DISTANCE ACROSS THE RIVER.

If $Y/W = 0.1$, then the pollutant concentration following incomplete mixing is 10 times higher than if complete mixing were to occur.

The distance L to complete mixing (see Figure IV-4) can be estimated (as an upper limit) by the following expression:

$$L_c = \frac{0.4\ W^2\ U}{\varepsilon_t} \qquad \text{(IV-6)}$$

where

L_c = distance below point source where complete mixing occurs
W = width of river
U = river velocity
ε_t = lateral diffusion coefficient

Values of the lateral diffusion coefficient can be estimated from the data given in Table IV-9. Also, the following predictive formula can be used:

$$\frac{\varepsilon_t}{Du^*} = \begin{cases} 0.1\text{-}0.2, \text{ for a straight rectangular flume} \\ 0.25, \text{ for irrigation channels} \\ 0.4\text{-}0.8, \text{ many natural channels} \end{cases} \qquad \text{(IV-7)}$$

where

D = mean depth of flow
u^* = friction velocity = $\sqrt{gDS}$
S = slope of channel

The actual distance L is probably less than that calculated from Equation IV-6 because of secondary mixing, river curvature, and initial momentum of the discharge. It is also sensitive to river width.

4.1.10 Water and Pollutant Balances

Many river systems are hydrologically complex. Flow patterns are influenced by tributaries, nonpoint sources of runoff, flow withdrawals, as well as point sources of pollution. If the planner intends to perform water quality analyses on a basin wide scale, it is probably prudent that a water

TABLE IV-9

EXPERIMENTAL MEASUREMENTS OF TRANSVERSE MIXING IN OPEN CHANNELS WITH CURVES AND IRREGULAR SIDES

Channel	Channel geometry	Channel width, W (m)	Mean depth of flow, d (m)	Mean velocity, $\overline{u}$ (m/s)	Shear velocity, u^* (m/s)	Transverse mixing coefficient (m^2/sec)	$\frac{\varepsilon_t}{Du^*}$
Missouri River near Blair, Nebraska	Meandering river	200	2.7	1.75	0.074	0.12	0.6
Laboratory	Smooth sides and bottom; 0.15 m long groins on both sides	2.2	0.097	0.11	-	-	0.36-0.49
	Smooth sides and bottom; 0.5 m long groins on both sides	2.2	0.097	0.11	-	-	0.3-0.4
Laboratory model of the IJssel River	Groins on sides and gentle curvature	1.22	0.9	0.13	0.0078	-	0.45-0.77
IJssel River	Groins on sides and gentle curvature	69.5	4.0	0.96	0.075	-	0.51
Mackenzie River from Fort Simpson to Norman Wells	Generally straight alignment or slight curvature; numerous island and sand bars	1240	6.7	1.77	0.152	0.67	3.4
Missouri River downstream of Cooper Nuclear station, Nebraska	Reach includes one 90° and one 180° bend	210-270	4	5.4	0.08	1.1	3.4
Potomac River; 29 km reach below the Dickerson Power Plant	Gently meandering river with up to 60° bends	350	0.73-1.74	0.29-0.58	0.033-0.051		0.52-0.65

from: Fischer, H.B., E.J. List, R.C.Y. Kob, J. Imberger, and N.H. Brooks, 1979. Mixing in Inland and oastal Waters. Adademic Press, New York.

budget be first completed. A water budget is a statement that

$$\frac{dS}{dt} = \sum \text{Inflows} - \sum \text{Outflows} = 0, \text{ for steady-state} \qquad \text{(IV-8)}$$

where

S = storage in the river channel

For the steady-state situations, which are examined here, the water budget simply states that inflows to the system equal outflows from the system. A water budget thus provides a method of determining whether the major flow contributions have been accurately assessed or not. If a large imbalance in the water budget exists, accurate evaluation of the major sources of pollutant might be difficult to achieve. An accurate water balance helps to minimize the possibility of inaccurate assessment of pollutant concentration. It does not eliminate the possibility.

Once a water balance has been completed, then a pollutant balance of a conservative pollutant can be developed based on the following relationship:

$$\sum_{\text{in}} \text{Flux} = \sum_{\text{out}} \text{Flux} \quad \text{,at steady-state} \qquad \text{(IV-9)}$$

where the fluxes are the rates of entry and loss of the pollutant into and out of the system, respectively. One of the following two expressions can be used to predict the mass loading rates:

$$M = 5.38\ C\ Q \qquad \text{(IV-10)}$$

where

M = mass loading rate, lbs/day

C = concentration, mg/l

Q = flow rate, ft^3/sec

and

$$M = 86.4\ C\ Q \qquad \text{(IV-11)}$$

where

M = mass loading rate, kgs/day

Q = flow rate, m^3/sec

When nutrient and water balances are developed, the following considerations should be kept in mind:

1. In most instances it is probably not possible to develop water or nutrient balances where inflows and outflows balance to within less than 10 percent of each other.

2. The system's upstream boundary must be included in the balance as a source and the downstream boundary as a loss.

3. All sources and losses should be mutually exclusive of each other.

4. Choose system boundaries to coincide with locations of gaging stations when possible.

5. Try to use comparable periods of record of data. This will help to minimize the impacts of trends which could be present in one record but not in another.

6. It is typically easier to develop water and mass balances on an annual basis, although balances can be developed for each season of the year. However, if the system is not at steady state, inflows and outflows _should_ _not_ balance.

Table IV-10 shows a suggested method of tabulating the results of water and pollutant balances. Total nitrogen (TN) and total phosphorus (TP) are the pollutants. All flow rates and loading rates are tabulated individually. Once total loading rates have been tabulated, the percent contribution from each source can be determined. Percent contributions help to determine the relative importances of each source as a contributor to pollution, and can provide a method to prioritize pollution abatement efforts.

TABLE IV-10

SUGGESTED CONFIGURATION FOR WATER AND NUTRIENT BALANCE TABLE

		Loading Rate			
Sources	Flow Rate	TN	%	TP	%
- Upstream - Tributaries - Irrigation Returns - Municipal - Industrial ⋮					
TOTAL					
Losses - Downstream - Diversions ⋮					
TOTAL					
$\frac{\text{Sources-Losses}}{\text{Losses}} \times 100$					

EXAMPLE IV-3

Figure IV-5 shows a hypothetical river which has three tributaries, a nonpoint source of runoff, and two diversions. Develop a water balance for this system. The known flow rates are

Identification Number	Flow rate (cfs)
1	2000
2	4000
3	1200
4	200
5	800
6	1000
7	2000
8	6000

The flowrates at locations 1,2,3, and 5 are assumed to comprise the inflow rates to the system. The total inflows are:

Identification Number	Inflows
1	2000 cfs
2	4000 cfs
3	1200 cfs
5	800 cfs
Total	8000 cfs

The inflow from gage 4 is not needed because gage 5 is located further downstream on the same tributary. The outflows consist of diversions 6 and 7 and the downstream outflow past gage 8:

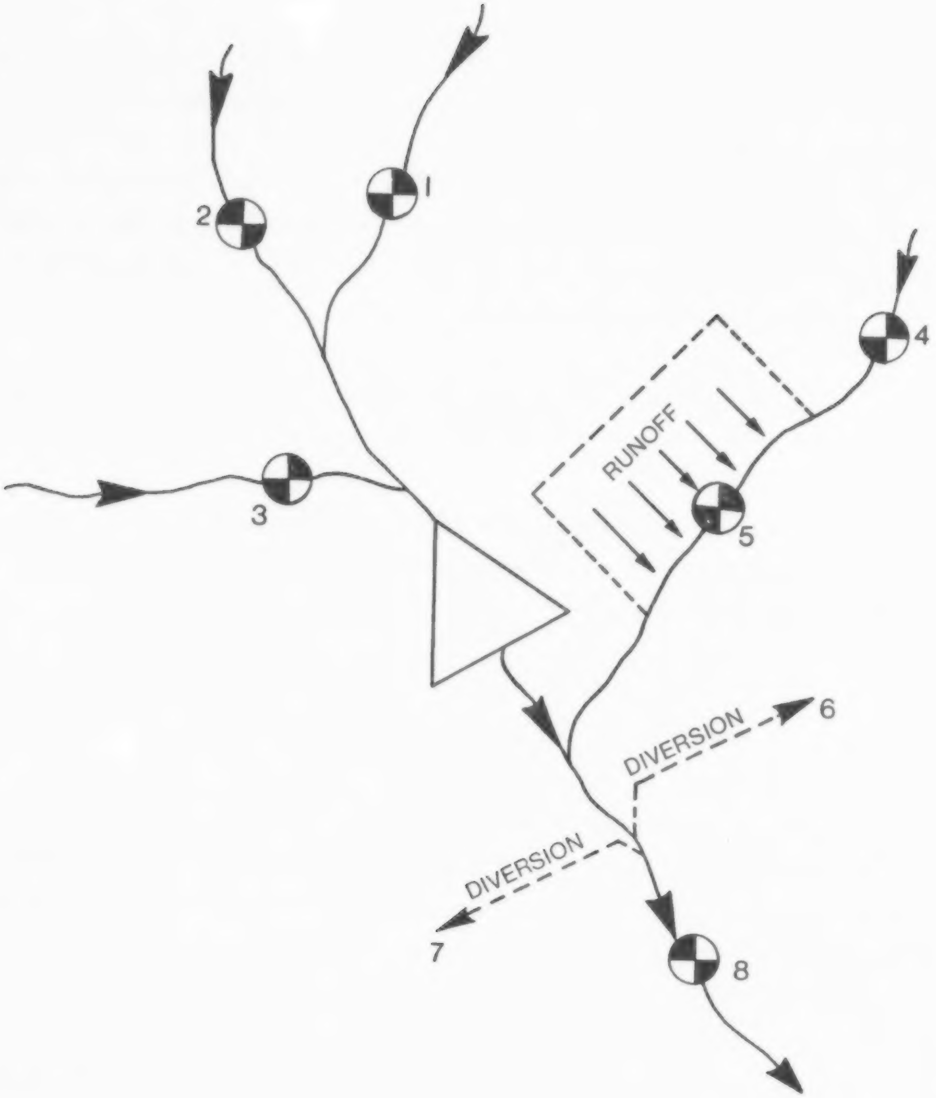

1
2
4
RUNOFF
3
5
6
DIVERSION
DIVERSION
7
8

FIGURE IV-5 ILLUSTRATION OF WATER BALANCE

Identification Number	Outflows
6	1000 cfs
7	2000 cfs
8	6000 cfs
	9000 cfs

The inflows and outflows differ by 1000 cfs. There are several reasons for the imbalance. One, the flow rate past each gage is not measured perfectly, but differs by some degree from the actual flow rate. Two, the gage at location 5 does not catch all of the nonpoint source runoff, so there is an additional inflow to the system which has not be quantified. Three, depending on the size of the reservoir, direct precipitation and evaporation might be significant.

END OF EXAMPLE IV-3

The following example illustrates both a water and nutrient balance, and is based on work performed by Tetra Tech on the Snake River in Idaho (Mills and Desvoigne, 1978).

EXAMPLE IV-4

Develop annual water and phosphorus balances for water year 1976 for the Snake River from Heise, Idaho, to below American Falls Reservoir, a distance of 150 miles. A sketch is shown in Figure IV-6. Estimate the phosphorus retention coefficient for American Falls Reservoir. The retention coefficient is defined as:

$$R_p = \frac{\text{Flux Input - Flux Output}}{\text{Flux Input}}$$

The required data are shown below.

- Surface area of American Falls Reservoir = 56,600 acres
- Evaporation rate in this part of United States = 33 inches/year

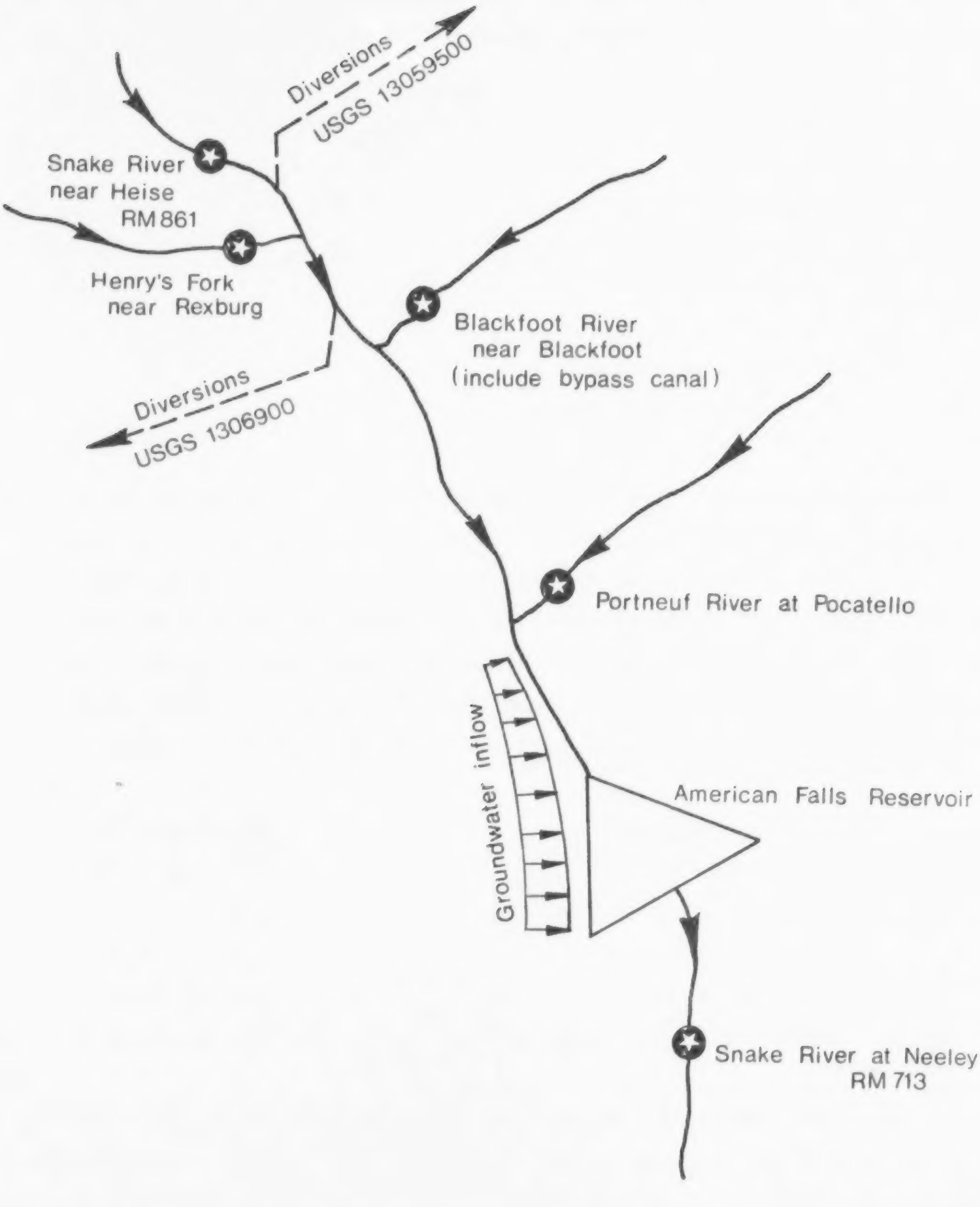

Diversions
USGS 13059500
Snake River
near Heise
RM 861
Henry's Fork
near Rexburg
Blackfoot River
near Blackfoot
(include bypass canal)
Diversions
USGS 1306900
Portneuf River at Pocatello
Groundwater inflow
American Falls Reservoir
Snake River at Neeley
RM 713

FIGURE IV-6 SKETCH OF SNAKE RIVER FROM HEISE TO NEELEY, IDAHO.

- Precipitation = 11 inches/year
- Ground water inflow into Snake River: 500 cfs
- Ground water inflow into American Falls Reservoir: 2,100 cfs.

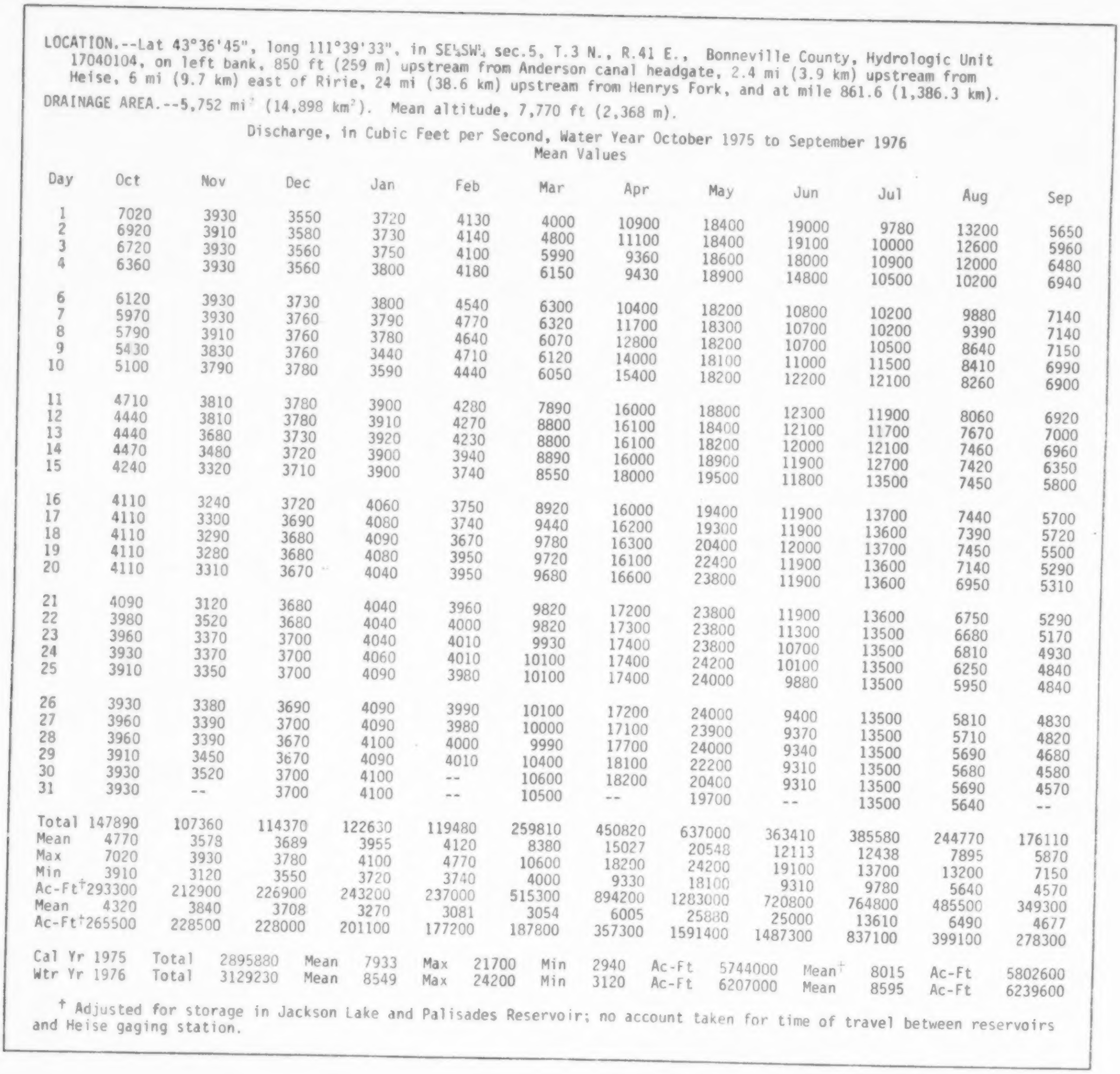
The total phosphorus concentrations were generated during the study of Mills and Desvoigne (1978) and are provided here:

Source	mg/l
In rainwater	0.03
Snake River near Heise	0.05
Henrys Fork	0.11
Blackfoot River	0.26
Portneuf River	0.68
Groundwater inflow	0.23
Snake River near Neeley	0.08

The surface inflow rates are gaged by the U.S. Geological Survey and are reported in the U.S. Geological Survey Water Data Report for Idaho (1976). An example of how the information is tabulated in these reports is shown in Figure IV-7. From an entry in the Table, the mean flow rate for water year 1976 is 8549 cfs at USGS 30307500, near Heise. Rather than showing the remaining tabulations from the USGS report the flow rates from water year 1976 will simply be tabulated, as contained in the report.

Source	Flow rate
Blackfoot River	453 cfs
Henrys Fork	3,235 cfs
Portneuf River	412 cfs
USGS 13059500 (diversion)	2,333,700 ac-ft/yr
USGS 13069000 (diversion)	800,900 ac-ft/yr

Based on this information the water and total phosphorus balances are calculated and shown in Table IV-11. The flow rates are all converted to units of cfs. This requires converting the precipitation, evaporation, and diversions to these units. A precipitation rate of 11 inches per year is equivalent to 71 cfs:



LOCATION.--Lat 43°36'45", long 111°39'33", in SE¼SW¼ sec.5, T.3 N., R.41 E., Bonneville County, Hydrologic Unit 17040104, on left bank, 850 ft (259 m) upstream from Anderson canal headgate, 2.4 mi (3.9 km) upstream from Heise, 6 mi (9.7 km) east of Ririe, 24 mi (38.6 km) upstream from Henrys Fork, and at mile 861.6 (1,386.3 km).

DRAINAGE AREA.--5,752 mi^2 (14,898 km^2). Mean altitude, 7,770 ft (2,368 m).

Discharge, in Cubic Feet per Second, Water Year October 1975 to September 1976
Mean Values

Day	Oct	Nov	Dec	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep
1	7020	3930	3550	3720	4130	4000	10900	18400	19000	9780	13200	5650
2	6920	3910	3580	3730	4140	4800	11100	18400	19100	10000	12600	5960
3	6720	3930	3560	3750	4100	5990	9360	18600	18000	10900	12000	6480
4	6360	3930	3560	3800	4180	6150	9430	18900	14800	10500	10200	6940
6	6120	3930	3730	3800	4540	6300	10400	18200	10800	10200	9880	7140
7	5970	3930	3760	3790	4770	6320	11700	18300	10700	10200	9390	7140
8	5790	3910	3760	3780	4640	6070	12800	18200	10700	10500	8640	7150
9	5430	3830	3760	3440	4710	6120	14000	18100	11000	11500	8410	6990
10	5100	3790	3780	3590	4440	6050	15400	18200	12200	12100	8260	6900
11	4710	3810	3780	3900	4280	7890	16000	18800	12300	11900	8060	6920
12	4440	3810	3780	3910	4270	8800	16100	18400	12100	11700	7670	7000
13	4440	3680	3730	3920	4230	8800	16100	18200	12000	12100	7460	6960
14	4470	3480	3720	3900	3940	8890	16000	18900	11900	12700	7420	6350
15	4240	3320	3710	3900	3740	8550	18000	19500	11800	13500	7450	5800
16	4110	3240	3720	4060	3750	8920	16000	19400	11900	13700	7440	5700
17	4110	3300	3690	4080	3740	9440	16200	19300	11900	13600	7390	5720
18	4110	3290	3680	4090	3670	9780	16300	20400	12000	13700	7450	5500
19	4110	3280	3680	4080	3950	9720	16100	22400	11900	13600	7140	5290
20	4110	3310	3670	4040	3950	9680	16600	23800	11900	13600	6950	5310
21	4090	3120	3680	4040	3960	9820	17200	23800	11900	13600	6750	5290
22	3980	3520	3680	4040	4000	9820	17300	23800	11300	13500	6680	5170
23	3960	3370	3700	4040	4010	9930	17400	23800	10700	13500	6810	4930
24	3930	3370	3700	4060	4010	10100	17400	24200	10100	13500	6250	4840
25	3910	3350	3700	4090	3980	10100	17400	24000	9880	13500	5950	4840
26	3930	3380	3690	4090	3990	10100	17200	24000	9400	13500	5810	4830
27	3960	3390	3700	4090	3980	10000	17100	23900	9370	13500	5710	4820
28	3960	3390	3670	4100	4000	9990	17700	24000	9340	13500	5690	4680
29	3910	3450	3670	4090	4010	10400	18100	22200	9310	13500	5680	4580
30	3930	3520	3700	4100	--	10600	18200	20400	9310	13500	5690	4570
31	3930	--	3700	4100	--	10500	--	19700	--	13500	5640	--
Total	147890	107360	114370	122630	119480	259810	450820	637000	363410	385580	244770	176110
Mean	4770	3578	3689	3955	4120	8380	15027	20548	12113	12438	7895	5870
Max	7020	3930	3780	4100	4770	10600	18200	24200	19100	13700	13200	7150
Min	3910	3120	3550	3720	3740	4000	9330	18100	9310	9780	5640	4570
Ac-Ft†	293300	212900	226900	243200	237000	515300	894200	1283000	720800	764800	485500	349300
Mean	4320	3840	3708	3270	3081	3054	6005	25880	25000	13610	6490	4677
Ac-Ft†	265500	228500	228000	201100	177200	187800	357300	1591400	1487300	837100	399100	278300

Cal Yr 1975	Total	2895880	Mean	7933	Max	21700	Min	2940	Ac-Ft	5744000	Mean†	8015	Ac-Ft	5802600
Wtr Yr 1976	Total	3129230	Mean	8549	Max	24200	Min	3120	Ac-Ft	6207000	Mean	8595	Ac-Ft	6239600

† Adjusted for storage in Jackson Lake and Palisades Reservoir; no account taken for time of travel between reservoirs and Heise gaging station.

FIGURE IV-7 EXAMPLE OF FLOW RATE INFORMATION TABULATED IN U.S. GEOLOGICAL SURVEY'S WATER DATA REPORT

TABLE IV-11

SOLUTION TO SNAKE RIVER WATER AND PHOSPHORUS BALANCE PROBLEM

Sources	Flow Rate (cfs)	TP Loading (lbs/day)
Snake River at Heise	8,549	2,300.
Blackfoot River	453	1,915.
Henrys Fork	3,235	634.
Portneuf River	412	1,510.
Ground water inflow into Snake River	500	619.
Ground water inflow into American Falls Reservoir	2,100	2,600.
Precipitation on American Falls Reservoir	71	11.
$\sum$ Sources	15,320	9,589.

Losses	Flow Rate (cfs)	TP Loading (lbs/day)
USGS 13059500	3,214.	865
USGS 13069000	1,103	415
Snake River at Neeley	11,360.	4,890
Evaporation	215.	-
$\sum$ Losses	15,892.	6,170

For flow, $\left(\frac{\text{Losses-Sources}}{\text{Losses}}\right) 100 = 4\%$

$$11 \div 12 \times 56600 \times 43560 \div 366 \div 24 \div 3600 = 71 \text{ cfs}$$

The diverted flow in ac-ft/yr is converted to cfs as shown:

$$\text{USGS } 13059500: \quad 2333700 \times 43560 \div 366 \div 24 \div 3600 = 3214$$

The percent difference between inflow rates and outflow rates is 4 percent.

Based on these flow rates, and the concentrations of total phosphorus presented earlier, the sources and losses of total phosphorus can be tabulated. For example, the mass flux of total phosphorus flowing past Heise can be calculated using Equation IV-10:

$$M = 5.38 \times 8549 \times 0.05 = 2300 \text{ lbs/day}$$

Continuing in this manner, the sources and losses are as tabulated in Table IV-11. The large imbalance is caused by retention at American Falls Reservoir. The phosphorus loading to the reservoir is:

$$9589 - 865 - 415 = 8309 \text{ lbs/day}$$

Since the phosphorus leaving the reservoir is 4890 lbs/day, the retention coefficient is:

$$R_p = \frac{8309 - 4890}{8309} = .41$$

American Falls Reservoir retains a significant quantity of the phosphorus which enters the reservoir and consequently tends to keep phosphorus levels in the Snake River below the dam depressed compared with what they would otherwise be.

END OF EXAMPLE IV-4

4.1.11 Hand Held Calculator Programs

It has become apparent that, after applying the river screening techniques contained in the original manual (Zison *et al*., 1977) to real systems, a substantial savings of both time and effort could be realized by programming the major computational sequences. To this end, these algorithms have been programmed on the Texas Instrument TI-59 calculator and are available upon request in a document prepared by Tetra Tech (Mills *et al*., 1979)*. To date the algorithms contained in Mills *et al*. (1979) predict:

- equilibrium temperature
- longitudinal instream temperature distribution
- mixing temperatures
- BOD profiles for point and nonpoint sources
- reaeration rates
- dissolved oxygen profiles
- waste assimilative capacity and critical dissolved oxygen levels
- coliform profiles for point and nonpoint sources
- bed material sediment transport

For each program contained in the document the following information is provided for the user:

- a detailed set of user instructions,
- a program listing, and
- a sample input/output sequence.

An example set of users instruction is shown in Figure IV-8. The first 6 steps are for data entry and the seventh is for calculation of the required information.

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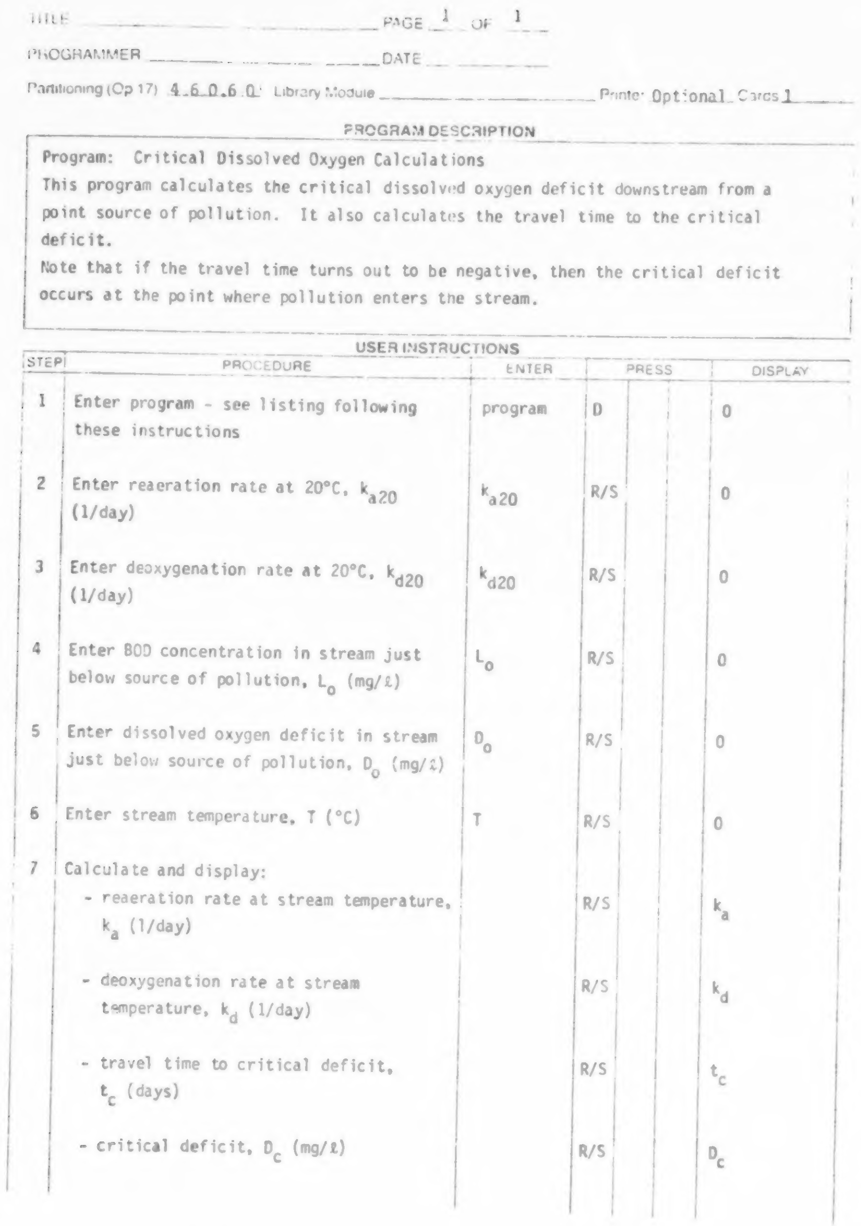
* Attention: W.B. Mills
Tetra Tech, Inc.
3746 Mt. Diablo Blvd., Suite 300
Lafayette, California 94549



TITLE ______ PAGE 1 OF 1

PROGRAMMER ______ DATE ______

Partitioning (Op 17) 4 6 0 6 0 Library Module ______ Printer Optional Cards 1

PROGRAM DESCRIPTION

Program: Critical Dissolved Oxygen Calculations

This program calculates the critical dissolved oxygen deficit downstream from a point source of pollution. It also calculates the travel time to the critical deficit.

Note that if the travel time turns out to be negative, then the critical deficit occurs at the point where pollution enters the stream.

USER INSTRUCTIONS

STEP	PROCEDURE	ENTER	PRESS	DISPLAY
1	Enter program - see listing following these instructions	program	D	0
2	Enter reaeration rate at 20°C, k_{a20} (1/day)	k_{a20}	R/S	0
3	Enter deoxygenation rate at 20°C, k_{d20} (1/day)	k_{d20}	R/S	0
4	Enter BOD concentration in stream just below source of pollution, L_o (mg/ℓ)	L_o	R/S	0
5	Enter dissolved oxygen deficit in stream just below source of pollution, D_o (mg/ℓ)	D_o	R/S	0
6	Enter stream temperature, T (°C)	T	R/S	0
7	Calculate and display:			
	- reaeration rate at stream temperature, k_a (1/day)		R/S	k_a
	- deoxygenation rate at stream temperature, k_d (1/day)		R/S	k_d
	- travel time to critical deficit, t_c (days)		R/S	t_c
	- critical deficit, D_c (mg/ℓ)		R/S	D_c

FIGURE IV-8 EXAMPLE SET OF USER'S INSTRUCTIONS FOR HAND HELD CALCULATOR PROGRAMS

4.2 CARBONACEOUS AND NITROGENOUS OXYGEN DEMAND

4.2.1 Introduction

Many wastes discharged into waterways contain biologically oxidizable materials that exert an oxygen demand on waterway resources. This biochemical oxygen demand (BOD) can be subdivided into carbonaceous (CBOD) and nitrogenous (NBOD) components. Table IV-12 illustrates typical concentrations of NBOD and CBOD in untreated municipal waste.

CBOD represents the amount of oxygen required by bacteria to stabilize organic matter under aerobic conditions. The reaction can be approximated by

$$C_nH_aO_bN_c + \left(n + \frac{a}{4} - \frac{b}{2} - \frac{3}{4}c\right) O_2 \rightarrow nCO_2 + \left(\frac{a}{2} - \frac{3}{2}c\right) H_2O + cNH_3 \qquad \text{(IV-12)}$$

This reaction assumes that the available organic matter is completely oxidized. Bacteria, however, might not be able to completely oxidize all of the available organic matter. Equation IV-13 does illustrate that oxidation of the nitrogen is not included as part of CBOD. The reduced nitrogen is oxidized to nitrate in a two step process as follows:

$$2NH_3 + 3O_2 \xrightarrow[\text{bacteria}]{\text{nitrite-forming}} 2NO_2^- + 2H^+ + 2H_2O \qquad \text{(IV-13)}$$

$$2NO_2^- + O_2 + 2H^+ \xrightarrow[\text{bacteria}]{\text{nitrate-forming}} 2NO_3^- + 2H^+ \qquad \text{(IV-14)}$$

Based on Equations IV-13 and IV-14 the NBOD is

$$\text{NBOD} = 4.57\left(\left[\text{Org-N}\right] + \left[NH_4^+ - N\right]\right) + 1.14\left[NO_2^- - N\right] \qquad \text{(IV-15)}$$

Typically the nitrite concentration is negligible so that

$$\text{NBOD} = 4.57\ (\text{TON}) \qquad \text{(IV-16)}$$

where TON represents total oxidizable nitrogen, the sum of organic and ammonia nitrogen. A typical value of TON from Table IV-12 is 20 + 28 = 48 mg-N/l, which corresponds to an NBOD of 220 mg/l.

TABLE IV-12

MUNICIPAL WASTE CHARACTERISTICS BEFORE TREATMENT (THOMANN, 1972)

Variable	Unit	Approx. Average	Normal Range
Average Daily Flow	gal/cap/day	125	100-200
Solids			
Total	mg/l	800	450-1200
Total Volatile	mg/l	400	250-800
Total Dissolved	mg/l	500	300-800
Total Suspended	mg/l	300	100-400
Volatile Suspended	mg/l	130	80-200
Settleable	mg/l	150	-
BOD			
Carbonaceous (5 day)	mg/l	180	100-450
Carbonaceous (ultimate)	mg/l	220	120-580
Nitrogenous*	mg/l	220	-
Nitrogen			
Total	mg/l N	50	15-100
Organic	mg/l N	20	5-35
Ammonia	mg/l N	28	10-60
Nitrite + Nitrate	mg/l N	2	0-6
Phosphate			
Total	mg/l PO_4	20	10-50
Ortho	mg/l PO_4	10	5-25
Poly	mg/l PO_4	10	5-25
Coliforms			
Total	million org./100 ml	30	2-50
Fecal	million org./100 ml	4	0.3-17

*Ultimate, Nitrogenous oxygen demand, exclusive of CBOD.

Typically in the bottle determination of CBOD and NBOD, the carbonaceous demand precedes the nitrogenous demand by 5 to 10 days, as shown in Figure IV-9. This had led workers to believe that nitrification can be ignored in river environments below a source of pollution up to a distance corresponding to a travel time of five to ten days. Such an assumption might be invalid for several reasons. Given that there are numerous sources of pollution along many rivers a viable population of nitrifying bacteria may already be present within the water column. Second, nitrifers can grow attached to the bottom substrate. Consequently, significant numbers can exist just below the discharge location and nitrification can proceed immediately. Nitrification by attached bacteria is more likely to be of significance in relatively shallow, wide rivers, which have stable bottom substrate (Mills, 1976).

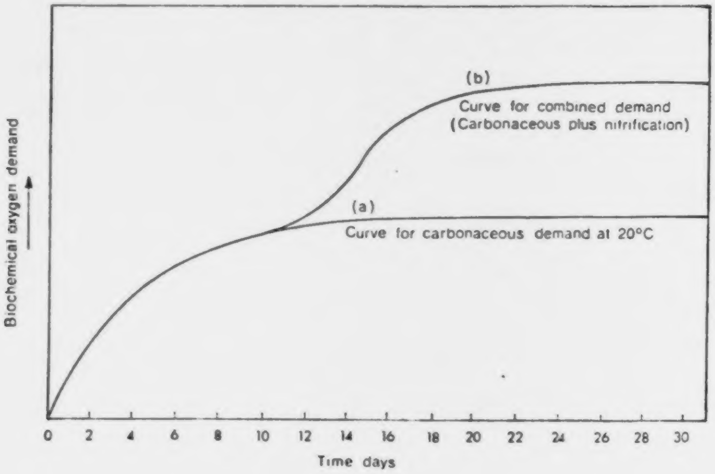


FIGURE IV-9 THE BOD CURVE. (A) CURVE FOR OXIDATION OF CARBONACEOUS MATTER. (B) CURVE SHOWING INFLUENCE OF NITRIFICATION.

CBOD is a commonly measured characteristic of waste water. The CBOD used in the formulations presented below is the ultimate CBOD. Often CBOD is expressed as $CBOD_5$, the oxygen utilized in a 5 day test. The relationship between ultimate ($CBOD_L$) and 5-day CBOD can be approximated by:

$$CBOD_L = \frac{CBOD_5}{0.68}$$

This relationship assumes a decay rate of 0.23/day, and may be different for effluents from advanced wastewater treatment plants.

The mass balance equation used in the CBOD analysis is exactly analogous to the NBOD equation. The first order decay rate assumption for NBOD stabilization is necessary to maintain this analogy, and is sufficient for hand calculations.

Nitrification (the process by which ammonia is oxidized to nitrite, and nitrite to nitrate) is pH dependent with an optimum range of 8.0 to 8.5 (Wild, 1971). If the pH of the river is below 7.0, nitrification is not likely to be important.

4.2.2 BOD Decay Rate

The decay rate for CBOD will be denoted by k_L and for NBOD by k_N. Typical values of both k_L and k_N lie between 0.1 and 0.6/day, with 0.3/day being typical. k_L values can, however, exceed the range given here. Values of 1 to 3/day have been computed for shallow streams (Thomann, 1972). A figure to be presented shortly will show how k_L depends on depth. The following discussion will be directed toward k_L, but in general will also apply to k_N.

The disappearance of BOD from a river is a reflection of both settling and biochemical oxidation, as shown in Figure IV-10. Biochemical oxidation can consist of instream oxidation (k_1L) as well as absorption by attached organisms (k_4L). The total oxidation rate then, is k_d, where

$$k_d = k_1 + k_4$$

The total loss rate k_L is

$$k_L = k_d + k_3$$

where k_3 reflects settling losses.

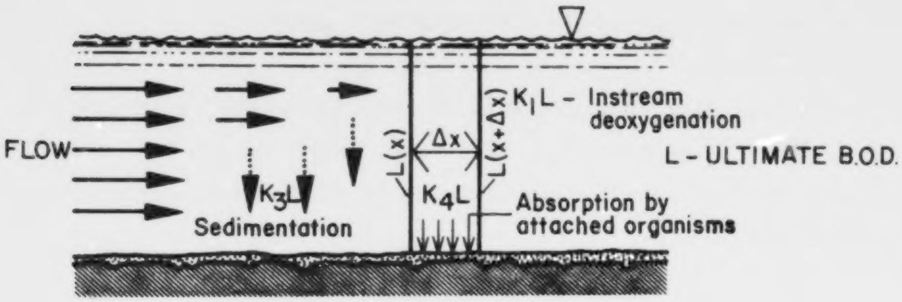


FIGURE IV-10 MECHANISMS OF BOD REMOVAL FROM RIVERS

Settling of BOD is generally more prevalent just below a sewage discharge where the discharged material may contain a large suspended fraction. As this material is transported downstream the settling component becomes less important and the reaction rate k_L approaches the oxidation rate k_d. In this chapter, the settling component will not be explicitly considered. Neglecting settling will tend to cause estimated instream BOD levels to be somewhat higher than they actually might be along certain portions of a river. It should be noted that if instream BOD data are used to determine k_L (one such method will be explained in Figure IV-12) then the effect of settling is automatically included in k_L.

Figure IV-11 illustrates the dependence of k_L on river depth. The highest deoxygenation rates occur in shallow streams with stable, rocky beds, reflecting the significance of attached biological organisms. Appendix C contains observed and predicted values of k_L for various natural streams.

The decay coefficients k_L and k_N are both temperature dependent and this dependence can be estimated by:

$$k_T = k_{20}\ 1.047^{(T-20)} \qquad \text{(IV-17)}$$

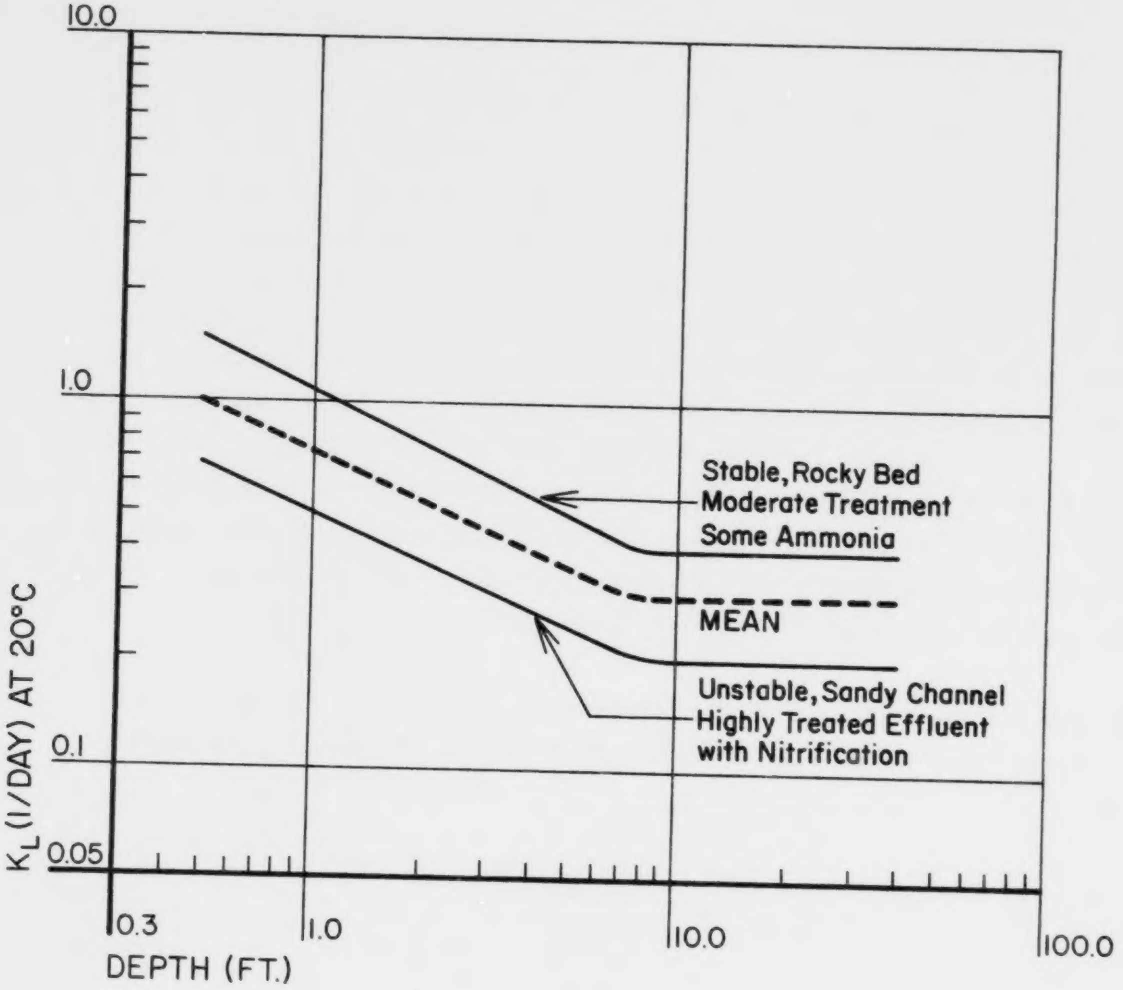


FIGURE IV-11 DEOXYGENATION COEFFICIENT AS A FUNCTION OF DEPTH, (AFTER HYDROSCIENCE, 1971)

where

k_{20} = k_L at 20^oC

k_T = k_L at T^oC

T = water temperature, ^oC

Numerous methods for computing k from observed data are available (Nemerow, 1974). One method entails the use of a semi-log plot. The stretch of river containing the data to be plotted must have a constant stream area and flow rate, and the BOD loading must be from a point source located at a position that will be called $x = 0$. Plotting the log of BOD concentration versus distance generally produces a straight line with slope of $-k_L/U$. An example is shown in Figure IV-12. Either $CBOD_5$ or $CBOD_L$ can be plotted as the ordinate. The slope should be converted from base 10 logarithms as given in the semi-log plot to base e logarithms as needed in the formulations used in this chapter. The conversion is made by multiplying the value for log base 10 by 2.303.

Wright and McDonnell (1979) have more recently developed an expression for instream BOD decay rate based on the flow rate of the river. The expression is:

$$k_d \left(\frac{1}{\text{day}}\right) = \begin{cases} k_{lab} & \text{if } Q>800 \text{ cfs} \quad \text{(IV-18a)} \\ \dfrac{10.3}{\sqrt{Q}} & \text{if } Q<800 \text{ cfs} \quad \text{(IV-18b)} \end{cases}$$

This expression is particularly attractive because the only hydraulic variable required is flow rate. Other predictive techniques and rate data from rivers around the country are contained in Zison _et al_. (1978).

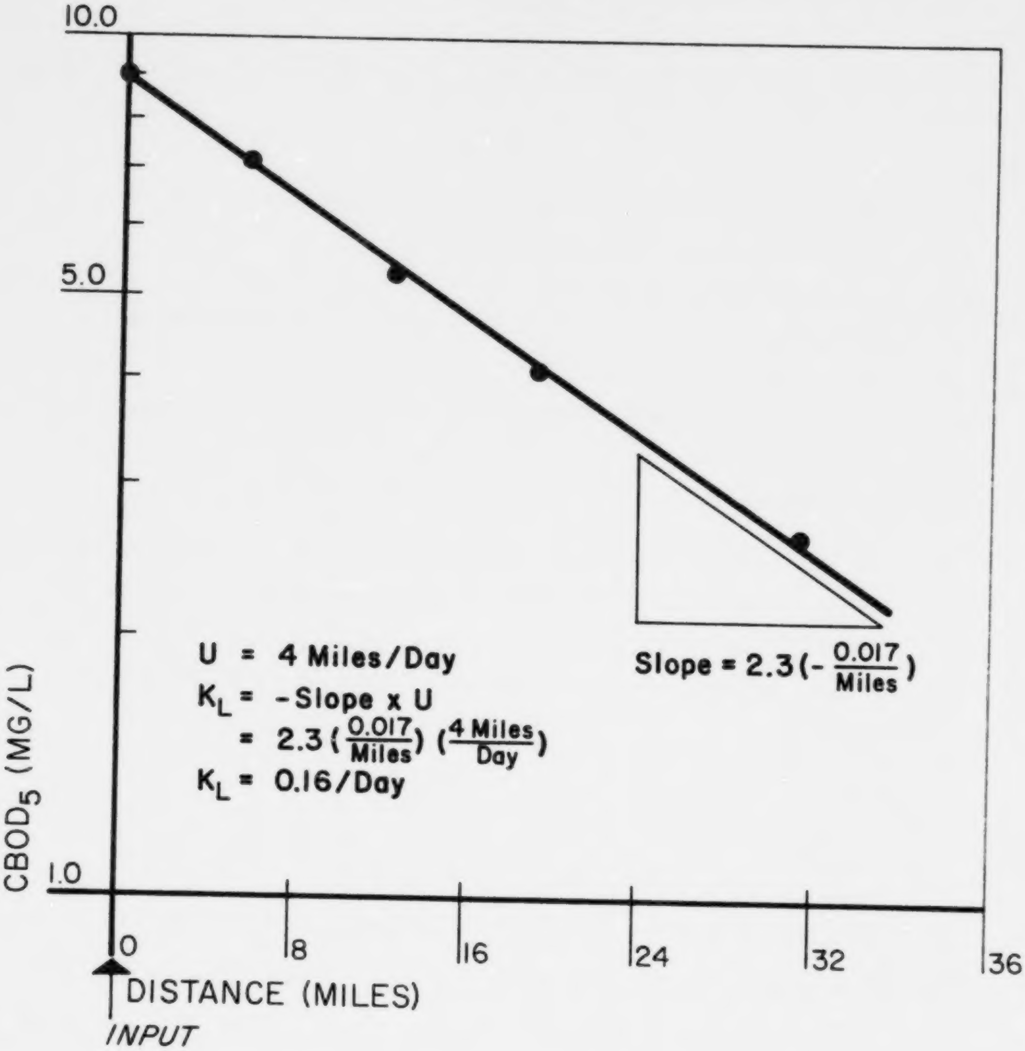


FIGURE IV-12 EXAMPLE OF COMPUTATION OF K_L FROM STREAM DATA (FROM HYDROSCIENCE, 1971)

4.2.3 Mass Balance of BOD

The general mass-balance equation for BOD in rivers is

$$\frac{\partial L}{\partial t} = 0 = \frac{-1}{A}\frac{\partial}{\partial x}(QL) - k_L L + L_r\left(\frac{\partial Q}{\partial x}\right)/A + L_{rd} \qquad \text{(IV-19)}$$

where

L = CBOD (ultimate) remaining to be oxidized, mg/l

Q = volumetric flow rate, ft^3/sec

A = cross-sectional area, ft^2

L_r = concentration of CBOD entering through an incremental sideflow (distributed source), mg/l

L_{rd} = mass flux of CBOD entering, with no associated flow, mg/l/sec

x = stream distance

$\frac{\partial L}{\partial t}$ = 0 indicates that steady-state conditions are being assumed and thus no accumulation of material takes place at any point within the reach.

The NBOD equation is completely analogous in form to Equation IV-19:

$$\frac{\partial N}{\partial t} = 0 = -\frac{1}{A}\frac{\partial}{\partial x}(QN) - k_N N + N_r\left(\frac{\partial Q}{\partial x}\right)/A + N_{rd} \qquad \text{(IV-20)}$$

where N is the NBOD.

N_{rd} represents purely a mass flux of nitrogenous material, while $N_r\left(\frac{\partial Q}{\partial x}\right)/A$ is a source of NBOD entering the river reach through an incremental sideflow. Thus, in cases where a known distributed source of BOD significantly contributes to a river reach under study, and the distributed flow (flow associated with a distributed source) can be neglected, N_{rd} can be used in lieu of $N_r\left(\frac{\partial Q}{\partial x}\right)/A$. N_{rd} can be estimated by determining the mass M of BOD entering a volume of river water V in time T. N_{rd} is given by:

$$N_{rd} = \frac{M}{VT}$$

For any particular reach of a river under investigation the stream cross-sectional area can be expressed by:

$$A = A_o + \left(\frac{A_f - A_o}{x_L}\right) x = A_o + \Delta_A x \qquad \text{(IV-21)}$$

where

$$\Delta_A = \frac{A_f - A_o}{x_L}$$

A_o = stream cross-sectional area at upstream end of the reach
A_f = stream cross-sectional area at downstrean end of reach
x = distance downstream from beginning of reach
x_L = length of reach

The cross-sectional area need not be measured directly, but can be computed from:

$$A = \frac{Q}{U}$$

The cross-sectional area change can reflect a change in stream velocity, perhaps due to a bed slope increase or decrease. The length of the reach under investigation, x_L, is measured in river miles along the river's centerline. If use of a constant stream area is assumed, then $\Delta_A = 0$ and $A = A_0$ throughout the reach.

4.2.4 Typical Solutions

Case 1: The only source of CBOD occurs as a point source at $x = 0$. The CBOD distribution is then expressed by:

$$L = L_o \exp\left[\frac{-j_L}{A_o}\left(A_o x + \Delta_A \frac{x^2}{2}\right)\right] \qquad \text{(IV-22)}$$

where

$$j_L = \frac{k_L}{U_o}$$

U_o = stream velocity at x = 0
L_o = ultimate BOD at the upstream end of the reach
L = ultimate BOD at a distance x downstream

The other terms have previously been defined. The initial CBOD, L_o, must reflect both CBOD upstream of the reach as well as that contributed by the point source in question. It is given by:

$$L_o = \frac{L_u Q_u + W/5.38}{Q_u + Q_W} \qquad \text{(IV-23)}$$

where

W = mass rate of discharge of CBOD, lb/day
Q_u = upstream river flow, cfs
Q_W = waste flow rate, cfs
L_u = upstream CBOD concentration, mg/l

Case 2: For a point source of CBOD at x = 0 and a distributed mass influx of CBOD (with no associated flow) entering the river throughout the reach, the solution is

$$L = \frac{L_{rd}}{k_L} + \left(L_o - \frac{L_{rd}}{k_L}\right) \exp\left[\frac{-j_L}{A_o}\left(A_o x + \Delta_A \frac{x^2}{2}\right)\right] \qquad \text{(IV-24)}$$

where

L_{rd} = mass rate of CBOD entering the reach per unit volume of river water, mg/l/day

Case 3: A distributed flow enters the river carrying CBOD and a point source of CBOD exists at x = 0. The flow rate Q at a distance x is:

$$Q = Q_o + \frac{Q_f - Q_o}{x_L} x = Q_o + \Delta_Q x$$

where

$$\Delta_Q = \frac{Q_f - Q_o}{x_L}$$

The BOD distribution is given by (the river cross-sectional area is assumed constant throughout the reach):

$$L = \frac{L_r}{E_1} + \left(L_o - \frac{L_r}{E_1}\right)\left(\frac{Q_o}{Q}\right)^{E_1} \tag{IV-25}$$

where

$$E_1 = \frac{k_L\ A_o + \Delta_Q}{\Delta_Q}$$

L_r = concentration of CBOD entering the river in the distributed flow, mg/l

Case 3 can also be used to establish the effect a purely diluting inflow (i.e. $L_r = 0$) would have on the CBOD distribution.

Case 4: For a point source at x = 0, a distributed source with associated inflow, and a mass flux with no associated flow (constant river cross-sectional area), the solution is

$$L = L_o\left(\frac{Q_o}{Q}\right)^{E_1} + \frac{L_r\Delta_Q + L_{rd}A_o}{k_L A_o + \Delta_Q}\left(1 - \left(\frac{Q_o}{Q}\right)^{E_1}\right) \tag{IV-26}$$

where

$$E_1 = \frac{k_L\ A_o + \Delta_Q}{\Delta_Q}$$, as in Case 3.

4.2.5 Other Simplifying Procedures

The formulations represented by Equations IV-22 through IV-26 offer a range of options for examining BOD distribution in rivers. However, there are additional methods of estimating instream concentrations and determining whether or not significant BOD levels exist.

Perhaps the simplest method is assuming that BOD does not decay. An upper limit of the instream concentration at any point can then be determined by incorporating all known sources, and using the methods presented in Section 4.7. If the computed instream concentrations are below a threshold pollution level, then there is no need to apply Equations IV-22 through IV-26 because the inclusion of a decay rate will only lower the concentrations.

It may also be feasible, as a first estimate, to combine the CBOD and NBOD equations into one, and use that equation to estimate the distribution of the total oxygen-demanding material. To do this, all source terms must include both CBOD and NBOD. One decay coefficient is used for both CBOD and NBOD decay. The larger decay coefficient of the two should be used since that will produce the larger oxygen deficit.

In deciding which of Equations IV-22 through IV-26 to use for any analysis, the purpose of the analysis as well as data availability should be considered. If the main purpose is to estimate differences in stream concentrations caused by various levels of abatement at a sewage treatment plant, the diffuse sources of BOD need not be considered. The resulting concentration difference can be expressed as:

$$\Delta L = \begin{cases} \Delta L_o \exp\left[\dfrac{-j_L}{A_o}\left(A_o x + \Delta_A \dfrac{x^2}{2}\right)\right] & \text{(IV-27a)} \\[2ex] \Delta L_o \left(\dfrac{Q_o}{Q}\right)^{E_1} & \text{(IV-27b)} \end{cases}$$

where ΔL is the change in BOD concentration due to a change, ΔL_o, in the initial concentration. Equation IV-27A should be used for a Case 1 or Case 2 situation, and Equation IV-27B for Case 3 or Case 4. If an estimate of the absolute level of BOD is desired, however, then the appropriate expression including the nonpoint sources should be utilized. It should be noted that if the diffuse sources of BOD are large then the improvement of instream BOD concentrations by point source control will be relatively minor. In that case the planner should focus on nonpoint source control.

EXAMPLE IV-5

Estimating BOD Distribution in a River

Suppose the user wants to calculate the BOD distribution in the river shown below in Figure IV-13. There are nine point sources contributing

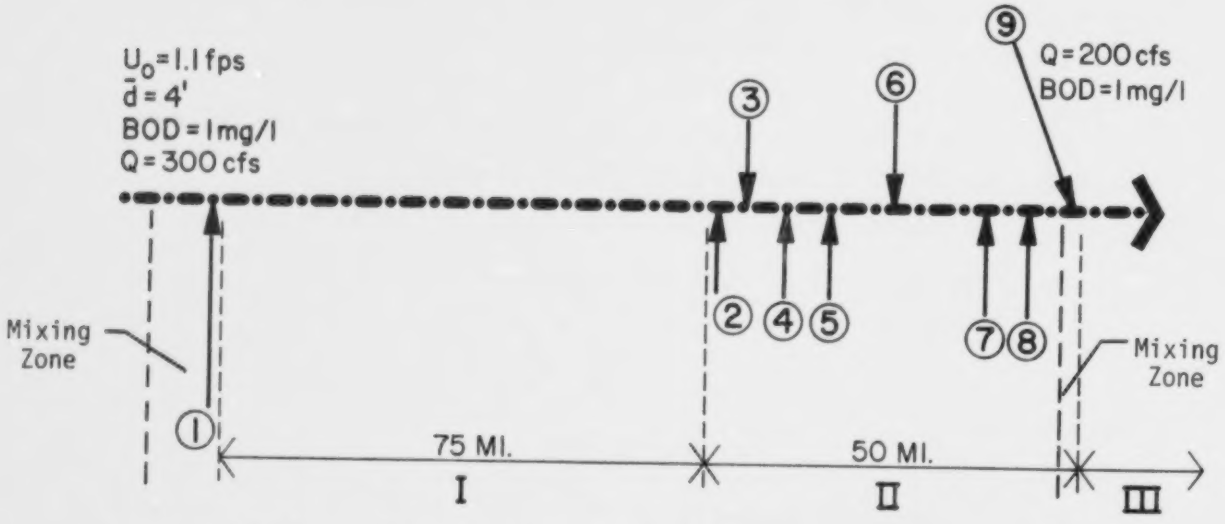

U_0=1.1 fps
$\bar{d}$ = 4'
BOD = 1 mg/l
Q = 300 cfs
⑨
Q = 200 cfs
BOD = 1 mg/l
③
⑥
②
④
⑤
⑦
⑧
Mixing Zone
①
Mixing Zone
75 MI.
50 MI.
I
II
III

FIGURE IV-13 HYPOTHETICAL BOD WASTE LOADINGS IN A RIVER

BOD in the stretch of river under consideration. The ninth source is assumed to be a tributary, and contributes substantially more flow than the other eight. Begin by dividing the river into reaches. The first reach (I) should include the first 75 miles in which there is one point source of BOD at the upstream end (source (1)). Equation IV-22 is applicable to that reach. Now, there are several choices available regarding the division of the river between sources (2) and (8). One choice is to divide the 50 miles into mini-reaches similar to reach I, and reapply Equation IV-22 seven more times. A second alternative is to group adjacent point sources into fewer and larger sources, thereby requiring fewer applications of Equation IV-22. A third alternative is to assume that sources (2) through (8) comprise one continuous distributed source, the total pollutant loading of this equivalent source being equal to the sum of the individual loads. For this representation to be valid the sources should be both evenly spread spatially and be discharging comparable loads. The third alternative will be examined here, and reach II will consist of the 50 miles following reach I. Equation IV-25 will be used to analyze reach II. Reach III then, will begin just downstream from the tributary (source (9)).

For reach I, Equation IV-22 is first solved. Suppose the following characteristics of waste source (1) are known:

$Q = 20 \text{ MGD} = 1.55\ (20) \text{ cfs} = 31 \text{ cfs}$

$W = 5000 \text{ lb. BOD}_5\text{/day}$

Recall that

$$L_o = \frac{L_u Q_u + W/5.38}{Q_u + Q_W}$$

W must be in lb. BOD ultimate/day:

$$W = \frac{5000}{.68} = 7353 \text{ lb. BOD}_L\text{/day}$$

Then

$$L_o = \frac{(1)\ (300) + 7353/5.38}{300 + 31} = 5.0 \text{ mg/l}$$

The decay coefficient is estimated from Figure IV-11 as 0.4/day. No correction will be made for temperature. Equation IV-22 can now be expressed as (for constant cross-sectional area):

$$L = 5 \exp\left(\frac{-0.4}{(1.1)(24)(3600)}\, x\right)$$

where x is the downstream distance in feet. Note the correction needed to convert the decay coefficient from units of 1/day to 1/sec.

The results of the above equation for selected distances downstream can be expressed as follows:

x (miles)	L (mg/l)
0	5.0
30	2.6
60	1.3
75	0.9

For reach II, sources (2) through (8) are assumed to contribute the following loading.

BOD = 8000 lb/day

Q = 120 MGD = 186 cfs

The flow distribution, Q, in reach II is then:

$$Q = Q_o + \frac{Q_f - Q_o}{x_L}\, x = 331 + \frac{186}{50}\, x$$

where x is in miles (from 0 to 50). L_r, the average BOD_L concentration in the incoming flow is:

$$L_r = \frac{8000 \text{ lb/day}}{120 \text{ MGD}} \times \frac{1 \text{ mg/l}}{8.34 \text{ lb/day}} = 8.0 \text{ mg/l}$$

If the average depth in reach II is assumed to be 5 feet, then:

$$k_L = .3/\text{day}$$

Finally, E_1 is computed:

$$E_1 = \frac{k_L A_o + \Delta_Q}{\Delta_Q}, \quad A_o = \frac{Q_o}{U_o} = \frac{331}{1.1} = 301 \text{ ft}^2$$

$$E_1 = \frac{\dfrac{(0.3)(301)}{(24)\ (3600)}}{\dfrac{186}{(50)(5280)}} + 1 = 2.5$$

Then, using L from the 75 mile point of Reach I as L_o:

$$L = \frac{8.0}{2.5} + \left(0.9 - \frac{8.0}{2.5}\right)\left(\frac{331}{Q}\right)^{2.5}$$

$$= 3.2 - 2.3\left(\frac{331}{Q}\right)^{2.5}$$

In tabulated form:

x (mi)	Q (cfs)	L (mg/l)
0	331	0.9
20	405	1.8
40	480	2.3
50	517	2.5

Note that the BOD concentration is increasing within this reach.

For reach III, only enough information is given to compute the initial concentration, utilizing weighted values for the BOD at the end of reach II and that entering through the tributary (source (9)).

$$L_o = \frac{200(1) + 517(2.5)}{200 + 517} = 2.1 \text{ mg/l}$$

END OF EXAMPLE IV-5

4.2.6 Interpretation of Results

The most frequent use of BOD data in river water quality analyses involves their relationship with the dissolved oxygen balance. This relationship will be discussed more fully in Section 4.3. At this point it is sufficient to say that it is necessary to predict the BOD distribution in a river in order to compute dissolved oxygen concentrations.

When a river receives a heavy load of organic matter, the normal processes of self purification result in a series of zones of decreasingly severe conditions succeeding one another downstream. Each zone contains characteristic animals and plants (Nemerow, 1974). A saprobicity system (saprobicity is a measure of biodegradable organic matter) has been developed that relates BOD concentrations in streams to the degree of pollution there. Correlations have been found, for example, among BOD concentrations, coliform bacteria, and dissolved oxygen in rivers (Sladecek, 1965). Sladecek (1969) has assigned 5-day BOD values of 5 mg/l to mildly polluted conditions and 10 mg/l to substantial pollution.

Sources of drinking water are subject to restraints on the maximum allowable BOD that can be contained in raw water and still qualify as a drinking water source. Further, the degree of treatment of the raw water is dependent on the concentrations of certain constituents, such as BOD. One reference (HEC, 1975) has stated that water having a 5-day BOD over 4 mg/l, in combination with high levels of other constituents, represents a poor source of domestic water supply.

As discussed above, BOD in a river can come from a number of sources, both point and nonpoint. Although BOD reduction from point source might be easier to accomplish than from nonpoint sources, there is no guarantee that BOD levels will be substantially lowered.

4.3 DISSOLVED OXYGEN

4.3.1. Introduction

Historically dissolved oxygen has been and continues to be the single most frequently used indicator of water quality in streams and rivers. Figure IV-14 shows the seasonal variability of dissolved oxygen in 22 major waterways throughout the country (EPA, 1974) from 1968 to 1972. Invariably the levels observed from June to October are lower than those observed in January to March. This is due primarily to the influence of temperature on the dissolved oxygen levels. Due to the effect of temperature, summer is the most critical season in terms of organic pollutant assimilation in rivers.

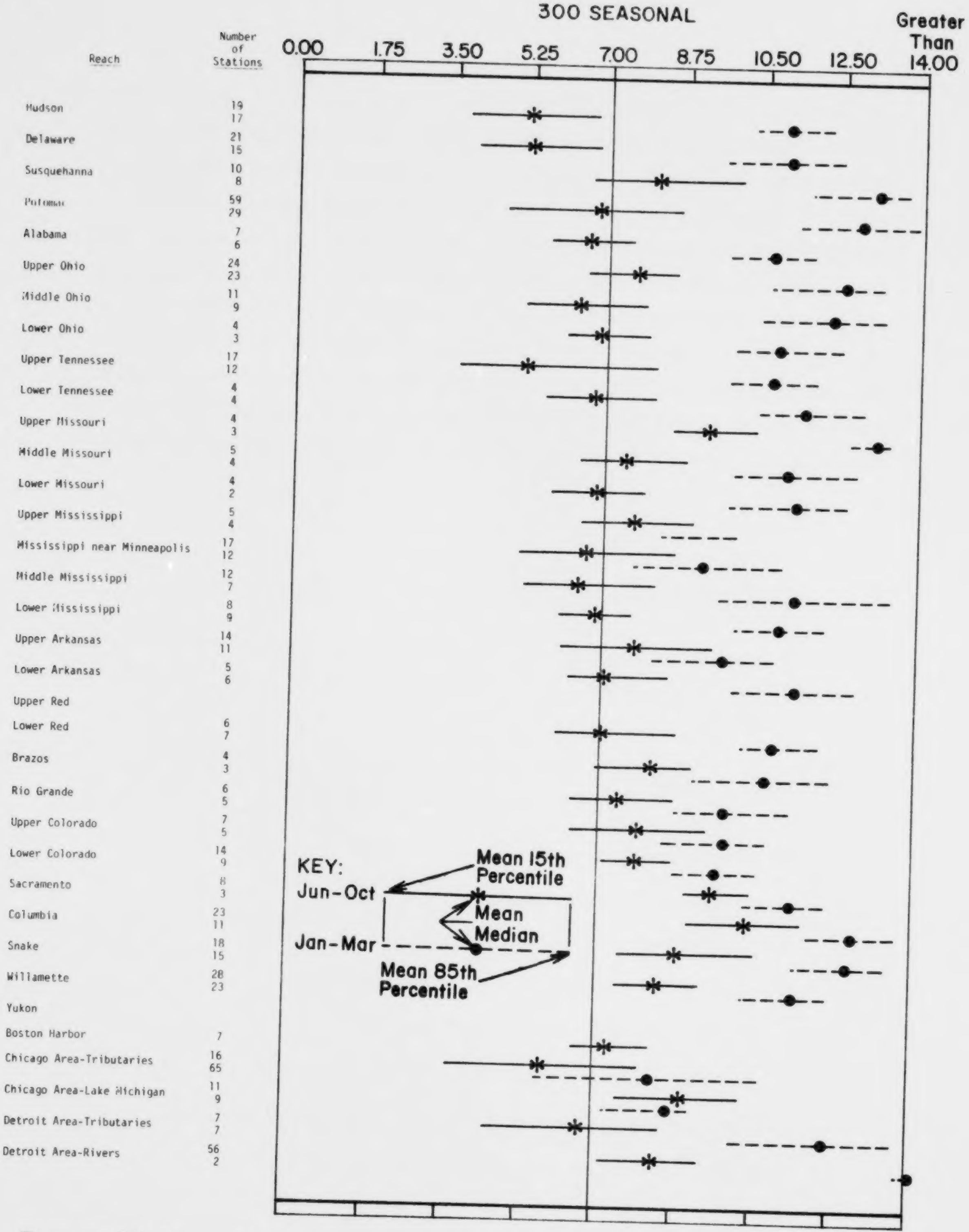


FIGURE IV-14 VARIABILITY OF DISSOLVED OXYGEN BY SEASON FOR 22 MAJOR WATERWAYS, 1968-72 (EPA, 1974)

The dissolved oxygen calculations presented below range in complexity from a simple CBOD-DO relationship to a more general dissolved oxygen mass balance including CBOD, NBOD, photosynthesis, respiration, and benthic demands. It should be stressed, however, that the results calculated from any of the relationships provide estimates only since each procedure incorporates various assumptions that might not be fully met. For example, waste loading inflows are assumed to remain constant in quality and quantity over time. In reality loadings probably vary over time. Furthermore the choice of system parameters involves a certain degree of judgment. However, for any given situation, the planner can establish an envelope of possible outcomes by different realistic choices of system parameters.

4.3.2 Dissolved Oxygen Mass-Balance

The general dissolved oxygen mass-balance equation that will be utilized here is given by:

$$\frac{\partial C}{\partial t} = 0 = - \frac{1}{A}\frac{\partial (QC)}{\partial x} - k_L L - k_N N + k_a (C_s - C) - S_b + P - R \qquad \text{(IV-28)}$$

where the new symbols introduced are:

C = dissolved oxygen concentration, mg/l

k_a = reaeration coefficient, 1/day

C_s = saturation value of dissolved oxygen, mg/l

S_b = benthic oxygen demand, mg/l/day

P = rate of oxygen production due to photosynthesis, mg/l/day

R = rate of oxygen consumption due to algal respiration, mg/l/day

Stated in words, Equation IV-24 expresses the following relationship:

At steady state, the rate of addition of dissolved oxygen to a river due to reaeration and photosynthesis equals the depletion rate caused by the net advective flow, carbonaceous oxidation, nitrogenous oxidation, benthic demands, and algal respiration.

Commonly, the dissolved oxygen mass-balance equation is expressed in terms of the deficit, D, which is the difference between the saturation and actual concentrations.

4.3.3 Reaeration Rate

The atmosphere acts as the major source for replenishing the dissolved oxygen resources of rivers. Reaeration tends to equilibrate the dissolved oxygen concentration in a river with its saturation value. Most commonly, the dissolved oxygen concentration is below saturation and there is a net influx of oxygen into the river from the atmosphere. On occasion, due to the production of dissolved oxygen by algae, rivers or streams can become supersaturated, in which case there is a net loss of oxygen to the atmosphere.

A number of expressions for the reaeration coefficient, k_a, have been developed. Several are presented here. O'Connor's formulation (Thomann, 1972) states that:

$$k_a = \frac{(D_L\ U)^{1/2}}{H^{3/2}} \text{ at } 20^{\circ}\text{C} \qquad \text{(IV-29)}$$

where

D_L = oxygen diffusivity = 0.000081 ft^2/hr at 20°C
H = stream depth in ft
U = stream velocity in ft/sec

Expressed in English units,

$$k_a = \frac{12.9\ U^{1/2}}{H^{3/2}} \text{ at } 20^{\circ}C \qquad \text{(IV-30)}$$

The above formula was verified on streams and rivers ranging in average depth from 1 foot to 30 feet with velocities ranging from 0.5 to 1.6 fps. Its use should be limited to streams where the reaeration coefficient is less than 12/day. Figure IV-15 illustrates how k_a changes with depth and velocity according to this relationship.

For shallow (0.4 - 2.4 feet), fast moving streams the following expression developed by Owens (Thomann, 1972) is preferable, as the experimental work to develop this expression was done almost exclusively on shallow streams:

$$k_a = 21.6 \frac{U^{0.67}}{H^{1.85}} \text{ at } 20^{\circ}C \qquad \text{(IV-31)}$$

where U is in ft/sec and H in feet. A graphical representation of Equation IV-31 is shown in Figure IV-16.

Covar (1976) showed that there were certain combinations of river depths and velocities where a formula developed by Churchill (Churchill et al., 1962) is more accurate than either the O'Connor or Owens formulations. The Churchill expression is:

$$k_a = 11.6U^{0.969}\ H^{-1.673} \text{ per day at } 20^{\circ}C \qquad \text{(IV-32)}$$

The regions of validity, and the predicted values, for the three formulations are shown in Figure IV-17.

Recent studies have suggested that the Owens expression overestimates the reaeration rate for particularly shallow streams (e.g., less than a foot in depth). Under these circumstances the Tsivoglou-Wallace method (Tsivoglou and Wallace, 1978) is more accurate. The expression is:

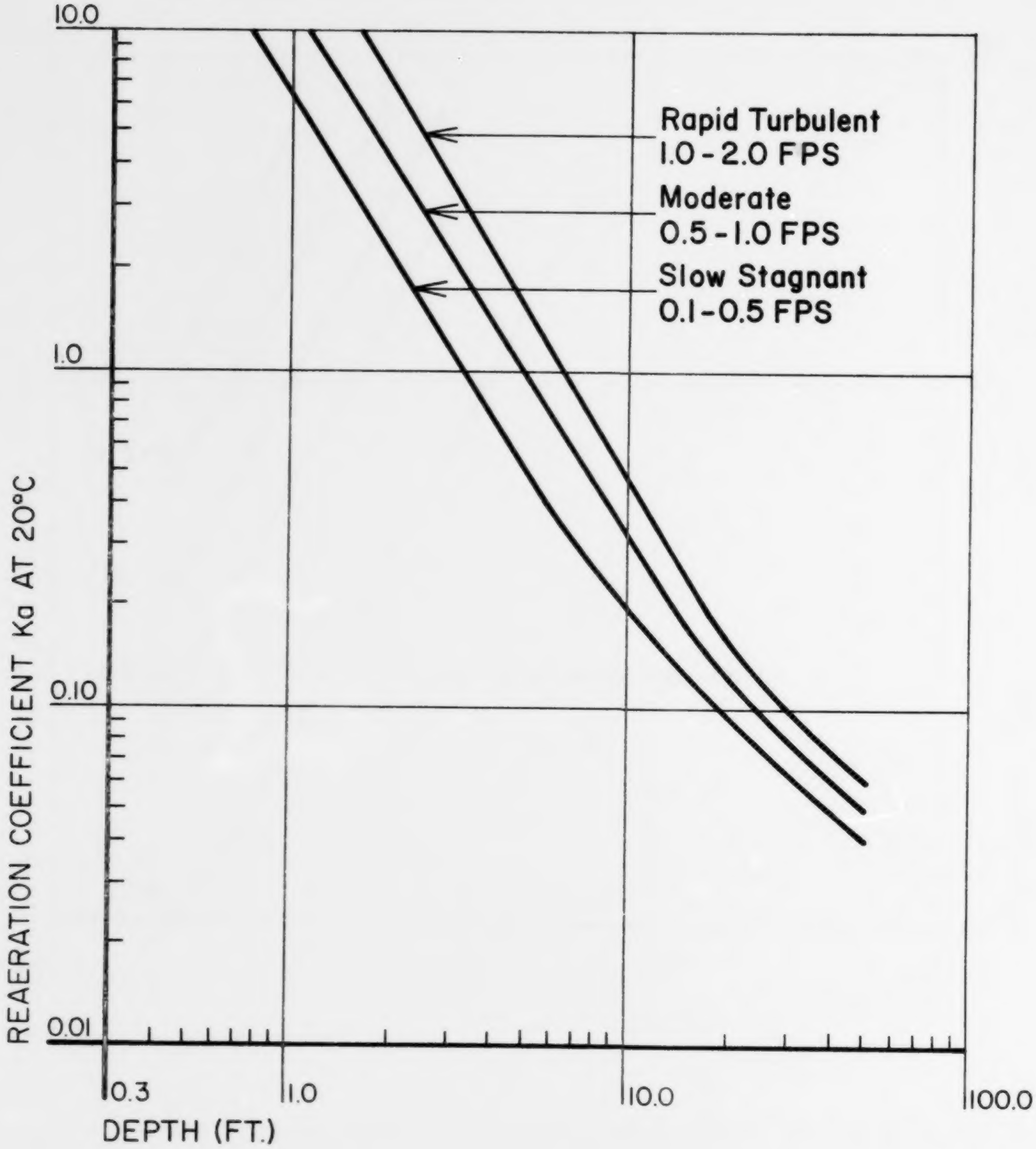


FIGURE IV-15 REAERATION COEFFICIENT AS A FUNCTION OF DEPTH (FROM HYDROSCIENCE, 1971)

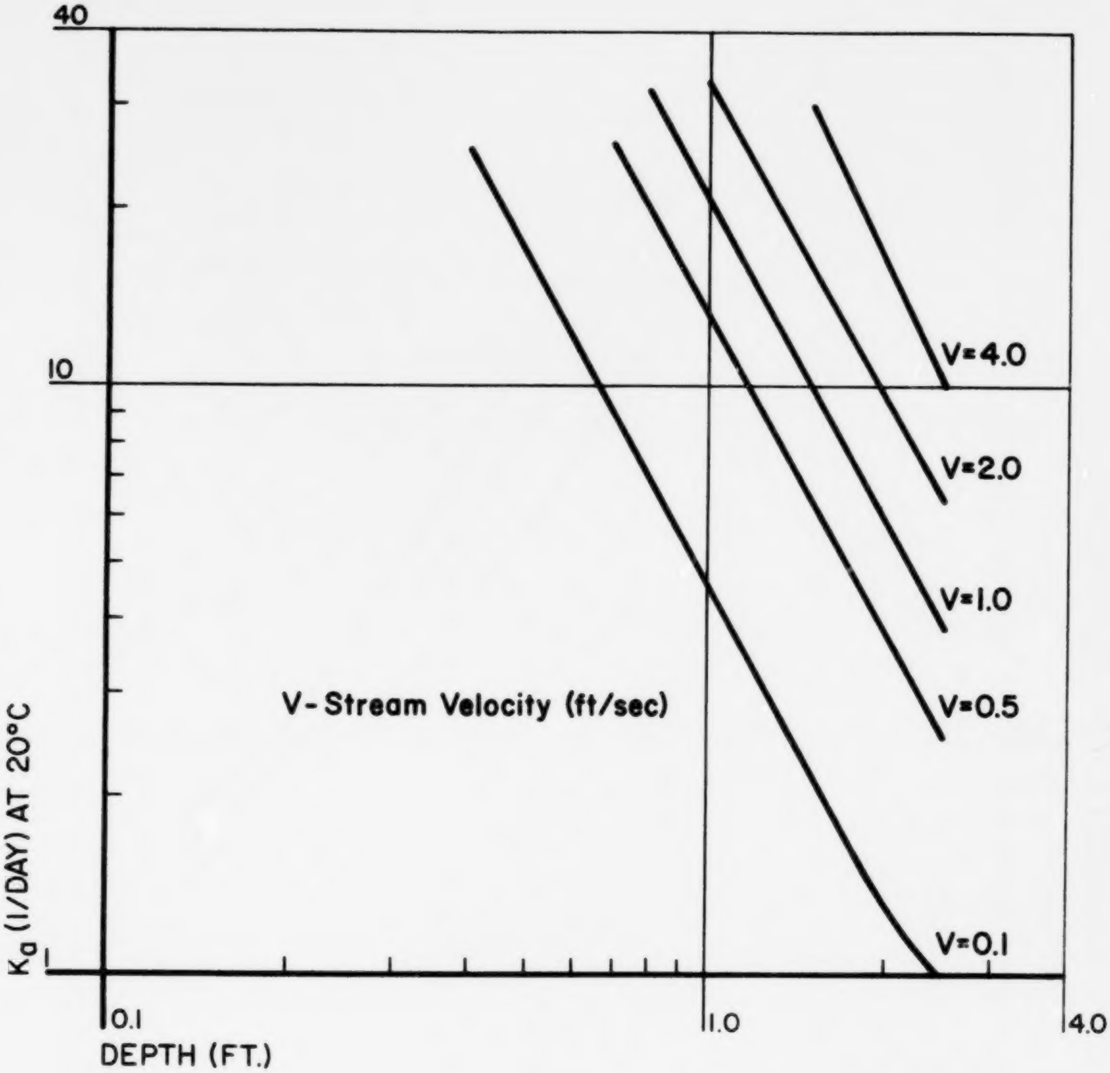


FIGURE IV-16 REAERATION COEFFICIENT FOR SHALLOW STREAMS, OWEN'S FORMULATION

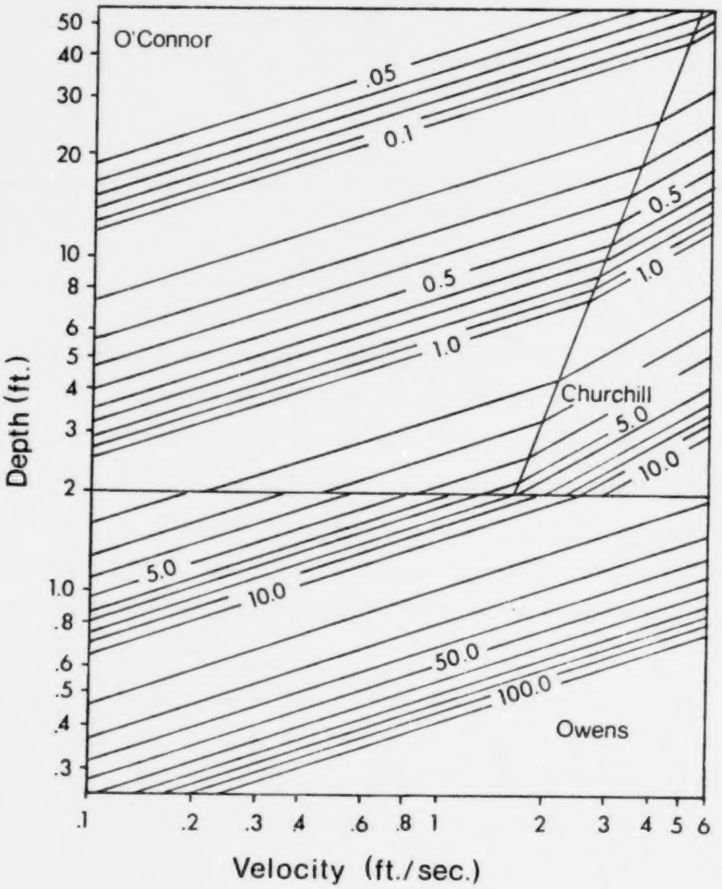


FIGURE IV-17 REAERATION RATE VERSUS DEPTH AND VELOCITY (FROM COVAR, 1976).

$$k_a \text{ (1/day)} = \begin{cases} 7776.\ US, @\ 25^{o}C,\ Q < 10 \text{ cfs} & \text{(IV-33a)} \\ 4665.6\ US, @\ 25^{o}C,\ 10 < Q < 3000 \text{ cfs} & \text{(IV-33b)} \\ 2592.\ US, @\ 25^{o}C,\ Q > 3000 \text{ cfs} & \text{(IV-33c)} \end{cases}$$

where

S = stream slope, ft/ft

Table IV-13 compares predictions of Tsivoglou-Wallace with observed values for several small streams in Wisconsin. The agreement is good.

EXAMPLE IV-6

Prediction of Reaeration Rates

In September, 1969, a study was conducted to determine the reaeration rate coefficients on the Patuxent River in Maryland during the low flow period. The study was carried out on a seven mile stretch of the river below Laurel, Maryland. The stream was divided into seven segments, and the reaeration rate determined for each segment. A portion of the results are shown in the Table IV-14. Using the hydraulic data in the table predict the reaeration rates using the methods of Tsivoglou-Wallace and of Covar.

Since the method of calculating the reaeration for each reach is the same, an example calculation will be shown for the first reach only. Based on a velocity of 0.39 ft/sec and a slope of 0.0013 ft/ft, the Tsivoglou-Wallace method predicts a reaeration rate of

$$k_a = 7776 \times 0.39 \times 0.0013 = 3.9\text{/day at } 25^{o}C$$

Equation IV-33a is used since Q<10 cfs.

Using Figure IV-17 and a river depth of 0.8 feet reveals that the Owens formula is applicable. Applying Equation IV-31 shows that

$$k_a = 21.6 \frac{0.39^{0.67}}{0.8^{1.85}} = 17.4\text{/day at } 20^{o}C$$

TABLE IV-13

COMPARISON OF PREDICTED AND OBSERVED REAERATION RATES ON SMALL STREAMS IN WISCONSIN*

Stream	Observed k_a (1/day at 25°C)	Predicted k_a Using Tsivoglou's Method (1/day at 25°C)
Black Earth Creek	8.46	7.8
Mud Creek tributary	10.7	4.2
Dodge Branch	33.1	34.6
Isabelle Creek	14.	-
Madison effluent channel	2.06	4.1
Mill Creek	3.31	2.2
Honey Creek	18.4	27.4
West Branch Sugar River	42.5	36.4
Koshkonong Creek	6.09	4.8
Badger Mill Creek	7.98	9.1

---

*Grant, R.S., 1976. Reaeration-Coefficient Measurements of 10 Small Streams in Wisconsin Using Radioactive Tracers... with a Section on the Energy-Dissipation Model. U.S. Geological Survey. Water Resources Investigations, 76-96.

TABLE IV-14

TYPICAL HYDRAULIC PROPERTIES
PATUXENT RIVER (SEPTEMBER, 1969)

Reach	Flow cfs	Length ft	Velocity ft/sec	Depth ft	Slope ft/ft	Reaeration Rate (1/day)		
						Observed (25°C)	Tsivoglou-Wallace (25°C)	Covar (20°C)
1-2	9.8	5,400	0.39	0.80	.0013	3.9		
2-3	9.8	4,200	0.22	1.00	.0011	2.7		
3-4	9.8	7,200	0.35	1.00	.0014	3.3		
4-5	19.5	8,400	0.35	1.10	.0018	3.5		
5-6	19.5	6,600	0.25	1.10	.0013	2.4		
6-7	19.5	4,800	0.37	1.00	.0013	4.8		

The results for all the reaches are tabulated below.

Reaeration Rate (1/day)

Reach	Observed (25°C)	Tsivoglou-Wallace (25°C)	Owens (20°C)
1-2	3.9	3.9	17.4
2-3	2.7	1.9	7.8
3-4	3.3	3.8	10.7
4-5	3.5	2.9	9.0
5-6	2.4	1.5	7.2
6-7	4.8	2.2	11.0

The predictions using the Tsivoglou-Wallace method are good for all reaches, while the method of Owens predict values two to three times too large, and provides evidence that Owens method probably should not be applied to extremely shallow rivers.

END OF EXAMPLE IV-6

Temperature changes affect the reaeration rate, and the relationship can be approximated by:

$$(k_a)_T = (k_a)_{20} \; 1.024^{(T-20)} \qquad \text{(IV-34)}$$

where

$(k_a)_T$ is the reaeration coefficient at T °C.

In addition to temperature, substantial suspended sediment concentrations can appreciably alter the reaeration rate in streams (Alonso et al., 1975). As an approximation, k_a decreases by 9 percent per 1,000 ppm increase in suspended sediment up to a 4,000 ppm load. Beyond that, concentration data are not available to assess the response of k_a. It is suggested that a 40 percent decrease be used for higher suspended sediment loads. Rivers with high suspended sediment loads are generally found in the western central states. Measured values of k_a for various streams and rivers are included in Appendix C.

4.3.4 Effect of Dams on Reaeration

Many rivers or streams have small to moderate sized dams crossing them in one or more places. Reaeration occurs as the water flows over the dam. Based on experimental data (Gameson _et al_., 1958), and later verified with field data (Barrett _et al_ 1960), the following relationship for reaeration over dams has been developed:

$$D_a - D_b = \left[1 - \frac{1}{1 + 0.11\ ab(1 + 0.046T)H}\right] D_a \qquad \text{(IV-35)}$$

where

D_a = dissolved oxygen deficit above dam, mg/l
D_b = dissolved oxygen deficit below dam, mg/l
T = temperature, ^oC
H = height through which the water falls, ft
a = 1.25 in clear to slightly polluted water: 1.00 in polluted water
b = 1.00 for weir with free fall: 1.3 for step weirs or cascades

An alternate equation developed from data on the Mohawk River and Barge Canal in New York State (Mastropietro, 1968) is as follows:

$$D_a - D_b = 0.037H\ D_a \qquad \text{(IV-36)}$$

Equation IV-36 is valid for dams up to fifteen feet high and for temperatures in the range of 20^o to 25^oC.

In handling the problem of a dam, a new reach can be started just below the dam. D_a can be calculated as the value that occurs at the end of the upstream reach. The new deficit D_b, which will become the deficit at the beginning of the next reach, is calculated using either of the above two formulas.

4.3.5 Dissolved Oxygen Saturation

The rate at which atmospheric reaeration occurs depends not only on k_a, but also on the difference between the saturation concentration C_s and the actual concentration C. The saturation value of dissolved oxygen is a function of temperature, salinity, and barometric pressure. The effect of salinity becomes important in esuarine systems, and to a lesser degree in rivers where high irrigation return flow can lead to substantial salinity values. Table IV-15 depicts the relationship between oxygen saturation and chlorinity. The expression relating salinity and chlorinity concentration is:

$$\text{Salinity } (^{o}/_{oo}) = 0.03 + 0.001805 \text{ chlorinity (mg/l)} \qquad \text{(IV-37)}$$

where

$^{o}/oo$ represents parts per thousand.

The temperature dependence (at zero salinity) can be expressed as:

$$C_s = 14.65 - 0.41022T + 0.00791T^2 - 0.00007774T^3 \qquad \text{(IV-38)}$$

where T is in ^{o}C. This relationship is also found in Table IV-15 for zero chloride concentration.

Barometric pressure affects C_s as follows:

$$\begin{aligned} C_s' &= C_s \left(\frac{P_b - P_v}{760-P_v}\right) \\ &\simeq C_s \left(1 - \frac{.027E}{760}\right) \end{aligned} \qquad \text{(IV-39)}$$

where

C_s = saturation value at sea level, at the temperature of the water, mg/l

C_s' = corrected value at the altitude of the river, mg/l

P_b = barometric pressure at altitude, mm Hg

TABLE IV-15

SOLUBILITY OF OXYGEN IN WATER (STANDARD METHODS, 1971)

Temp. in °C	Chloride Concentration in Water - mg/l					Difference per 100 mg Chloride
	0	5,000	10,000	15,000	20,000	
	Dissolved Oxygen - mg/l					
0	14.6	13.8	13.0	12.1	11.3	0.017
1	14.2	13.4	12.6	11.8	11.0	0.016
2	13.8	13.1	12.3	11.5	10.8	0.015
3	13.5	12.7	12.0	11.2	10.5	0.015
4	13.1	12.4	11.7	11.0	10.3	0.014
5	12.8	12.1	11.4	10.7	10.0	0.014
6	12.5	11.8	11.1	10.5	9.8	0.014
7	12.2	11.5	10.9	10.2	9.6	0.013
8	11.9	11.2	10.6	10.0	9.4	0.013
9	11.6	11.0	10.4	9.8	9.2	0.012
10	11.3	10.7	10.1	9.6	9.0	0.012
11	11.1	10.5	9.9	9.4	8.8	0.011
12	10.8	10.3	9.7	9.2	8.6	0.011
13	10.6	10.1	9.5	9.0	8.5	0.011
14	10.4	9.9	9.3	8.8	8.3	0.010
15	10.2	9.7	9.1	8.6	8.1	0.010
16	10.0	9.5	9.0	8.5	8.0	0.010
17	9.7	9.3	8.8	8.3	7.8	0.010
18	9.5	9.1	8.6	8.2	7.7	0.009
19	9.4	8.9	8.5	8.0	7.6	0.009
20	9.2	8.7	8.3	7.9	7.4	0.009
21	9.0	8.6	8.1	7.7	7.3	0.009
22	8.8	8.4	8.0	7.6	7.1	0.008
23	8.7	8.3	7.9	7.4	7.0	0.008
24	8.5	8.1	7.7	7.3	6.9	0.008
25	8.4	8.0	7.6	7.2	6.7	0.008
26	8.2	7.8	7.4	7.0	6.6	0.008
27	8.1	7.7	7.3	6.9	6.5	0.008
28	7.9	7.5	7.1	6.8	6.4	0.008
29	7.8	7.4	7.0	6.6	6.3	0.008
30	7.6	7.3	6.9	6.5	6.1	0.008
31	7.5					
32	7.4					
33	7.3					
34	7.2					
35	7.1					

P_v = saturation vapor pressure of water at the river temperature, mm Hg

E = elevation, feet

Table IV-16 illustrates the variability of dissolved oxygen saturation with altitude and temperature. The significant effect of altitude is apparent and should not be neglected. For example, at a temperature of 20°C, the saturation value decreases from 9.2 mg/l to 7.2 mg/l as the altitude increases from sea level to 6000 feet, the approximate elevation of Lake Tahoe and the Truckee River in California and Nevada.

4.3.6 DO-BOD Interactions

A widely used dissolved oxygen predictive equation is the Streeter-Phelps relationship which predicts the dissolved oxygen concentration downstream from a point source of BOD. Assuming a constant river cross-sectional area, the dissolved oxygen deficit (C_s-C) can be expressed as:

$$D = D_o \exp\left[\frac{-k_a x}{U}\right] + \frac{L_o k_L}{k_a - k_L}\left[\exp\left(\frac{-k_L x}{U}\right) - \exp\left(\frac{-k_a x}{U}\right)\right] \quad \text{(IV-40)}$$

where

k_a = reaeration coefficient, 1/day

D_o = initial deficit (at x = 0), mg/l

D = deficit at x, mg/l

L_o = initial BOD (at x = 0), mg/l

k_L = BOD decay coefficient, 1/day

L_o and D_o are found by proportioning BOD and DO deficit concentrations just upstream of the waste discharge with the influx from the discharge itself. As presented earlier in the BOD section, L_o is given by:

$$L_o = \frac{W/5.38 + L_u Q_u}{Q_w + Q_u} \quad \text{(IV-41)}$$

TABLE IV-16

DISSOLVED OXYGEN SATURATION VERSUS TEMPERATURE AND ALTITUDE

Temperature (°C)	ALTITUDE (ft)				
	0	2,000	4,000	6,000	8,000
0	14.6	13.6	12.5	11.5	10.5
5	12.8	11.9	11.0	10.1	9.2
10	11.3	10.5	9.7	8.9	8.1
15	10.2	9.5	8.8	8.0	7.3
20	9.2	8.5	7.9	7.2	6.6
25	8.4	7.8	7.2	6.6	6.0
30	7.6	7.1	6.5	6.0	5.4
35	7.1	6.6	6.1	5.6	5.1

where

W = discharge rate of BOD, lb/day

L_u = concentration of BOD in the river upstream of the waste discharge, mg/l

Q_u = river flow rate upstream of discharge, cfs

Q_w = flow rate of waste discharge, cfs

$Q_w + Q_u$ = flow rate of river in the reach under consideration, cfs

W in Equation IV-41 should be expressed in terms of ultimate BOD, and not 5-day BOD.

The initial deficit is found from:

$$D_o = C_s - \frac{C_w Q_w + C_u Q_u}{Q_w + Q_u} = \frac{D_w Q_w + D_u Q_u}{Q_w + Q_u} \qquad \text{(IV-42)}$$

where

C_w = concentration of dissolved oxygen in the waste, mg/l

C_u = concentration of dissolved oxygen upstream of the waste discharge, mg/l

D_w = dissolved oxygen deficit in waste, mg/l

D_u = dissolved oxygen deficit upstream, mg/l

In cases where information is lacking, D_o can normally be assumed to be in the range 1-2 mg/l.

If NBOD is to be considered as well as CBOD, Equation IV-40 can be modified as follows:

$$D = D_o \exp\left[\frac{-k_a x}{U}\right] + \frac{L_o k_L}{k_a - k_L}\left[\exp\left(\frac{-k_L x}{U}\right) - \exp\left(\frac{-k_a x}{U}\right)\right]$$

$$+ \frac{N_o k_N}{k_a - k_N}\left[\exp\left(\frac{-k_N x}{U}\right) - \exp\left(\frac{-k_a x}{U}\right)\right] \qquad \text{(IV-43)}$$

If the decay coefficient of NBOD is approximately equal to that of CBOD, Equation IV-40 can be utilized instead of the more complicated Equation

IV-43. In this case, L_o in Equation IV-40 is replaced by the sum of L_o and N_o.

4.3.7 Dissolved Oxygen Calculations

Calculation of dissolved oxygen in rivers can proceed as shown in Figure IV-19. The planner needs to estimate the waste loading scheme for the prototype, whether it be for a 20 year projection or for current conditions. The river system can then be divided into reaches and by repeated use of Equation IV-40, dissolved oxygen calculations can be performed for each reach, starting from a known boundary condition and proceeding downstream. All data and calculations should be succinctly and clearly recorded to minimize errors.

The dissolved oxygen profile downstream from a waste discharge characteristically has a shape shown in Figure IV-18. If the reach is

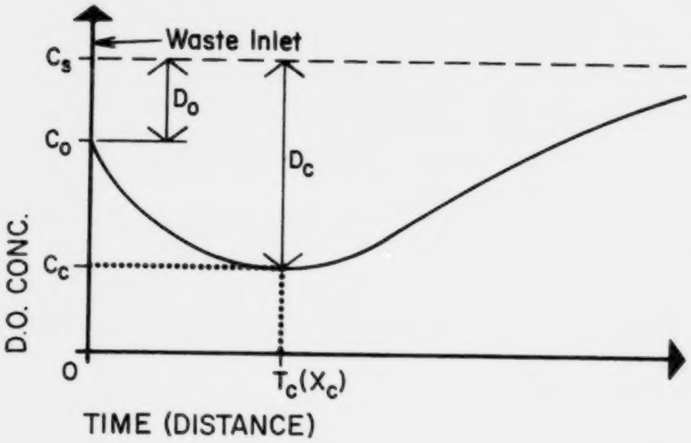


FIGURE IV-18 CHARACTERISTIC DISSOLVED OXYGEN PROFILE DOWNSTREAM FROM A POINT SOURCE OF POLLUTION

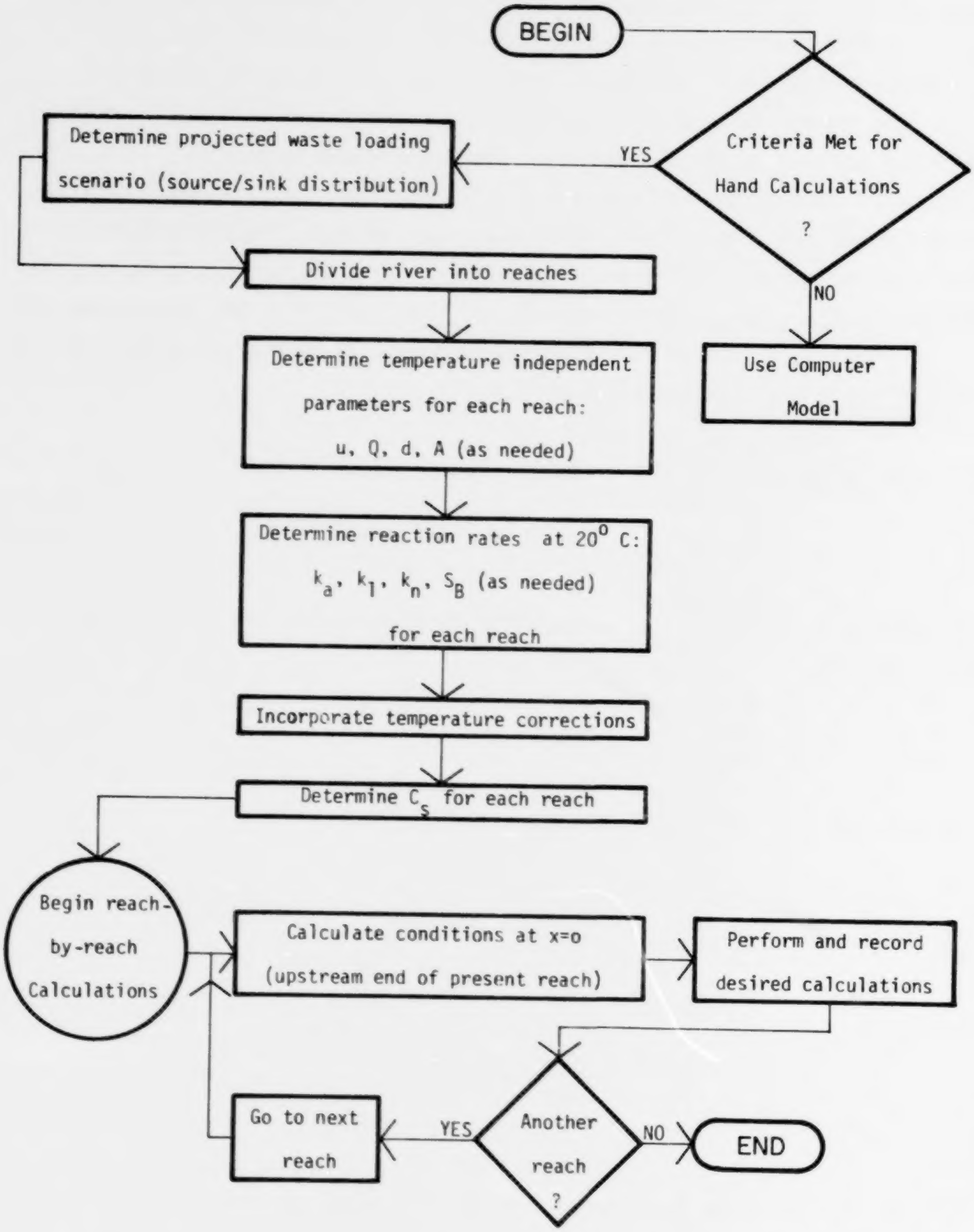

BEGIN
Criteria Met for Hand Calculations ?
YES
NO
Use Computer Model
Determine projected waste loading scenario (source/sink distribution)
Divide river into reaches
Determine temperature independent parameters for each reach: u, Q, d, A (as needed)
Determine reaction rates at 20° C: k_a, k_1, k_n, S_B (as needed) for each reach
Incorporate temperature corrections
Determine C_s for each reach
Begin reach-by-reach Calculations
Calculate conditions at x=o (upstream end of present reach)
Perform and record desired calculations
Another reach ?
YES
NO
Go to next reach
END

FIGURE IV-19 FLOW PROCESS OF SOLUTION TO DISSOLVED OXYGEN PROBLEM IN RIVERS

long enough, the dissolved oxygen deficit will increase to some maximum value, D_c, at a distance x_c (termed the critical distance). D_c is called the critical deficit. Within any reach there will always be a minimum dissolved oxygen value that occurs, but it may not be the critical deficit, which is defined as the minimum point on a dissolved oxygen sag. The difference between the minimum and critical values should be kept in mind. As one example of the difference between the values, a reach may have a dissolved oxygen profile where concentrations are monotonically decreasing throughout the reach. The minimum DO will then occur at the downstream end of the reach, but this will NOT be the critical DO value, since DO is still decreasing in the downstream direction.

The travel time to the critical deficit is given by:

$$t_c = \frac{1}{k_a - k_L} \ln \left[\frac{k_a}{k_L} \left(1 - \frac{D_o(k_a - k_L)}{k_L L_o} \right) \right] \qquad \text{(IV-44)}$$

The distance downstream can be computed by knowing the travel time and flow velocity:

$$x_c = U \cdot t_c \qquad \text{(IV-45)}$$

The critical deficit can be found from:

$$D_c = \left(D_o - \frac{L_o k_L}{k_a - k_L} \right) \left(\frac{k_a}{k_L} \left(1 - \frac{D_o(k_a - k_L)}{k_L L_o} \right) \right)^{\frac{-k_a}{k_a - k_L}} + \frac{L_o k_L}{k_a - k_L} \left[\frac{k_a}{k_L} \left(1 - \frac{D_o(k_a - k_L)}{k_L L_o} \right) \right]^{\frac{-k_L}{k_a - k_L}} \qquad \text{(IV-46)}$$

The formulas for the critical dissolved oxygen deficit are not really applicable in the special case when $k_a = k_L$. However, these special cases can readily be handled in one of two ways. First a small change can be made in either k_a or k_L so that k_a and k_L are approximately equal. Or second, the following expression can be used to predict critical travel time:

$$t_c = \frac{1}{k_a}\left(1 - \frac{D_o}{L_o}\right) \qquad \text{(IV-47)}$$

Then, the critical deficit is given by

$$D_c = \exp\left[\ln\left(\frac{k_L}{k_a} L_o\right) - k_L t_c\right] \qquad \text{(IV-48)}$$

Equation IV-48 is valid for all k_a/k_L values, and is not limited to cases where $k_a/k_L = 1$.

Solutions to both Equations IV-46 and IV-44 are presented in Tables IV-17 and IV-18, respectively. There exist practical limitations to the solutions of both equations, governed by the conditions that the solutions be both positive and real. If in solving Equation IV-44 t_c is negative, the minimum dissolved oxygen concentration actually occurs at the point of discharge, and concentrations increase immediately below the discharge.

Tables IV-17 and IV-18 are particularly useful for computing the waste assimilative capacity of a river. Waste assimilative capacity (WAC), as defined here, is the amount of BOD that can be discharged into a river without causing the minimum dissolved oxygen level to fall below a specified value. In constructing Tables IV-17 and IV-18 extra detail was incorporated for D_o/L_o values between 0.0 and 0.5. This is necessary because most practical problems fall within this range.

The following steps show how to use Table IV-17.

1. Find the reaeration rate (k_a) and the BOD decay rate (k_L) for the river being investigated.

2. Find the BOD concentration in the river just below the point of mixing (L_o).

3. Find the dissolved oxygen deficit at this location ($D_o = C_s - C$).

TABLE IV-17

D_c/L_o VALUES VERSUS D_o/L_o AND k_a/k_L

k_a/k_L

D_o/L_o	0.1	0.3	0.5	0.7	0.9	1.1	1.3	1.5	1.7	1.9	2.1	2.3	2.5	2.7	2.9	3.1	3.3	3.5	3.7	3.9	4.1	4.3	4.5	4.7	4.9
0.00	.77	.60	.50	.44	.39	.35	.32	.30	.28	.26	.24	.23	.22	.21	.20	.19	.18	.17	.17	.16	.15	.15	.14	.14	.14
0.02	.79	.61	.51	.44	.40	.36	.33	.30	.28	.26	.25	.23	.22	.21	.20	.19	.18	.18	.17	.16	.16	.15	.15	.14	.14
0.04	.81	.62	.52	.45	.40	.36	.33	.31	.29	.27	.25	.24	.23	.22	.21	.20	.19	1.8	.17	.17	.16	.16	.15	.15	.14
0.06	.82	.63	.53	.46	.41	.37	.34	.31	.29	.27	.26	.24	.23	.22	.21	.20	.19	.18	.18	.17	.17	.16	.15	.15	.15
0.08	.84	.65	.54	.47	.42	.38	.35	.32	.30	.28	.26	.25	.24	.23	.21	.21	.20	.19	.18	.18	.17	.16	.16	.15	.15
0.10	.85	.66	.55	.48	.43	.39	.36	.33	.31	.29	.27	.26	.24	.23	.22	.21	.20	.19	.19	.18	.17	.17	.16	.16	.15
0.12	.87	.67	.56	.49	.44	.40	.36	.34	.31	.29	.28	.26	.25	.24	.23	.22	.21	.20	.19	.19	.18	.17	.17	.16	.16
0.14	.88	.68	.57	.50	.45	.40	.37	.34	.32	.30	.28	.27	.25	.24	.23	.22	.21	.21	.20	.19	.19	.18	.18	.17	.17
0.16	.90	.69	.58	.51	.45	.41	.38	.35	.33	.31	.29	.27	.26	.25	.24	.23	.22	.21	.21	.20	.19	.19	.18	.18	.17
0.18	.91	.71	.59	.52	.46	.42	.39	.36	.33	.31	.30	.28	.27	.26	.25	.24	.23	.22	.21	.21	.20	.20	.19	.19	.19
0.20	.93	.72	.60	.53	.47	.43	.39	.37	.34	.32	.30	.29	.28	.26	.25	.24	.24	.23	.22	.22	.21	.21	.20	.20	.20
0.22	.95	.73	.62	.54	.48	.44	.40	.37	.35	.33	.31	.30	.28	.27	.26	.25	.25	.24	.23	.23	.22	.22			
0.24	.96	.75	.63	.55	.49	.45	.41	.38	.36	.34	.32	.31	.29	.28	.27	.26	.26	.25	.25	.24	.24				
0.26	.98	.76	.64	.56	.50	.46	.42	.39	.37	.35	.33	.31	.30	.29	.28	.27	.27	.26	.26						
0.28	.99	.77	.65	.57	.51	.47	.43	.40	.38	.36	.34	.32	.31	.30	.29	.29	.28	.28							
0.30	1.01	.78	.66	.58	.52	.48	.44	.41	.39	.37	.35	.34	.32	.31	.31	.30	.30								
0.32	1.03	.80	.67	.59	.53	.49	.45	.42	.40	.38	.36	.35	.34	.33	.32	.32									
0.34	1.04	.81	.68	.60	.54	.50	.46	.43	.41	.39	.37	.36	.35	.34	.34										
0.36	1.06	.82	.70	.61	.55	.51	.47	.44	.42	.40	.38	.37	.36	.36											
0.38	1.07	.84	.71	.62	.56	.52	.48	.45	.43	.41	.40	.39	.38												
0.40	1.09	.85	.72	.63	.57	.53	.49	.46	.44	.42	.41	.40													
0.42	1.11	.86	.73	.65	.58	.54	.50	.47	.45	.44	.43	.42													
0.44	1.12	.88	.74	.66	.60	.55	.51	.49	.47	.45	.44														
0.46	1.14	.89	.76	.67	.61	.56	.53	.50	.48	.47	.46														
0.48	1.15	.90	.77	.68	.62	.57	.54	.51	.49	.48															
0.50	1.17	.92	.78	.69	.63	.59	.55	.53	.51	.50															
0.6	1.25	.99	.84	.76	.69	.65	.62	.60																	
0.7	1.33	1.06	.91	.82	.76	.72	.70																		
0.8	1.41	1.13	.98	.89	.84	.81																			
0.9	1.50	1.20	1.05	.97	.92	.90																			
1.0	1.58	1.27	1.12	1.04	1.00																				
1.1	1.66	1.35	1.20	1.13	1.10																				
1.2	1.75	1.43	1.28	1.21																					
1.3	1.83	1.50	1.36	1.30																					
1.4	1.92	1.58	1.44	1.40																					
1.5	2.00	1.66	1.53																						
1.6	2.09	1.75	1.62																						
1.7	2.17	1.83	1.71																						
1.8	2.26	1.91	1.80																						
1.9	2.34	2.00	1.90																						
2.0	2.43	2.08																							
2.1	2.52	2.17																							
2.2	2.60	2.26																							

k_a/k_L

D_o/L_o	5.1	5.3	5.5	5.7	5.9	6.1	6.3	6.5	6.7	6.9	7.1	7.3	7.5	7.7	7.9	8.1	8.3	8.5	8.7	8.9	9.1	9.3	9.5	9.7	9.9
0.00	.13	.13	.12	.12	.12	.11	.11	.11	.11	.10	.10	.10	.10	.10	.09	.09	.09	.09	.09	.09	.08	.08	.08	.08	.08
0.02	.13	.13	.13	.12	.12	.12	.11	.11	.11	.11	.10	.10	.10	.10	.10	.09	.09	.09	.09	.09	.09	.08	.08	.08	.08
0.04	.14	.13	.13	.13	.12	.12	.12	.11	.11	.11	.11	.10	.10	.10	.10	.10	.09	.09	.09	.09	.09	.09	.08	.08	.08
0.06	.14	.14	.13	.13	.13	.12	.12	.12	.12	.11	.11	.11	.11	.10	.10	.10	.10	.10	.09	.09	.09	.09	.09	.09	.09
0.08	.15	.14	.14	.13	.13	.13	.12	.12	.12	.12	.11	.11	.11	.11	.11	.10	.10	.10	.10	.10	.10	.09	.09	.09	.09
0.10	.15	.15	.14	.14	.14	.13	.13	.13	.12	.12	.12	.12	.11	.11	.11	.11	.11	.11	.11	.10	.10	.10	.10	.10	.10
0.12	.16	.15	.15	.14	.14	.14	.14	.13	.13	.13	.13	.12	.12	.12	.12	.12	.12								
0.14	.16	.16	.16	.15	.15	.15	.14	.14	.14	.14	.14														
0.16	.17	.17	.17	.16	.16	.16																			
0.18	.18	.18	.18																						

TABLE IV-18

$k_a t$ VERSUS D_o/L_o AND k_a/k_L

	k_a/k_L																								
$\frac{D_o}{L_o}$	0.1	0.3	0.5	0.7	0.9	1.1	1.3	1.5	1.7	1.9	2.1	2.3	2.5	2.7	2.9	3.1	3.3	3.5	3.7	3.9	4.1	4.3	4.5	4.7	4.9
0.00	.26	.52	.69	.83	.95	1.05	1.14	1.22	1.29	1.36	1.42	1.47	1.53	1.58	1.62	1.67	1.71	1.75	1.79	1.83	1.87	1.90	1.93	1.97	2.00
0.02	.25	.51	.68	.82	.93	1.03	1.11	1.19	1.25	1.32	1.37	1.43	1.48	1.52	1.57	1.61	1.65	1.68	1.72	1.75	1.78	1.81	1.84	1.87	1.89
0.04	.25	.50	.67	.80	.91	1.00	1.08	1.16	1.22	1.28	1.33	1.38	1.42	1.47	1.50	1.54	1.57	1.61	1.64	1.66	1.69	1.72	1.74	1.76	1.78
0.06	.25	.50	.66	.79	.89	.98	1.06	1.13	1.18	1.24	1.29	1.33	1.37	1.41	1.44	1.47	1.50	1.53	1.55	1.57	1.59	1.61	1.63	1.65	1.66
0.08	.25	.49	.65	.78	.88	.96	1.03	1.09	1.15	1.20	1.24	1.28	1.31	1.35	1.37	1.40	1.42	1.44	1.46	1.48	1.49	1.50	1.51	1.52	1.53
0.10	.25	.49	.64	.76	.86	.94	1.00	1.06	1.11	1.16	1.19	1.23	1.26	1.28	1.30	1.32	1.34	1.35	1.36	1.37	1.38	1.38	1.38	1.38	1.38
0.12	.24	.48	.63	.75	.84	.92	.98	1.03	1.08	1.11	1.15	1.17	1.20	1.22	1.23	1.24	1.25	1.25	1.26	1.26	1.25	1.24	1.23	1.22	1.20
0.14	.24	.48	.63	.74	.82	.89	.95	1.00	1.04	1.07	1.10	1.12	1.13	1.15	1.15	1.16	1.16	1.15	1.14	1.13	1.11	1.09	1.07	1.04	1.00
0.16	.24	.47	.62	.72	.81	.87	.92	.97	1.00	1.03	1.05	1.06	1.07	1.07	1.07	1.07	1.05	1.04	1.02	.99	.96	.92	.88	.83	.77
0.18	.24	.47	.61	.71	.79	.85	.90	.93	.96	.98	1.00	1.00	1.00	1.00	.99	.97	.95	.92	.88	.84	.79	.73	.66	.57	.48
0.20	.24	.46	.60	.70	.77	.83	.87	.90	.92	.94	.94	.94	.93	.92	.90	.87	.83	.78	.73	.66	.59	.49	.39	.25	.09
0.22	.24	.45	.59	.68	.75	.80	.84	.87	.88	.89	.89	.88	.86	.83	.80	.76	.70	.64	.56	.46	.35	.21	.04		
0.24	.23	.45	.58	.67	.73	.78	.81	.83	.84	.84	.83	.81	.78	.74	.70	.64	.56	.47	.36	.23	.06				
0.26	.23	.44	.57	.66	.72	.76	.79	.80	.80	.79	.77	.74	.70	.65	.55	.50	.41	.28	.13						
0.28	.23	.44	.56	.64	.70	.74	.76	.76	.76	.74	.71	.67	.62	.55	.47	.36	.23	.07							
0.30	.23	.43	.55	.63	.68	.71	.73	.73	.72	.69	.65	.60	.53	.44	.34	.20	.03								
0.32	.23	.43	.54	.62	.66	.69	.70	.69	.67	.64	.59	.52	.44	.33	.20	.02									
0.34	.23	.42	.54	.61	.65	.67	.67	.66	.63	.58	.52	.44	.34	.21	.04										
0.36	.22	.42	.53	.59	.63	.65	.64	.62	.58	.53	.45	.36	.23	.07											
0.38	.22	.41	.52	.58	.61	.62	.61	.58	.54	.47	.38	.27	.12												
0.40	.22	.41	.51	.57	.60	.60	.58	.55	.49	.41	.31	.18													
0.42	.22	.41	.50	.56	.58	.58	.55	.51	.44	.35	.23	.08													
0.44	.22	.40	.49	.54	.56	.55	.52	.47	.39	.29	.15														
0.46	.22	.40	.49	.53	.54	.53	.49	.43	.34	.23	.07														
0.48	.22	.39	.48	.52	.53	.51	.46	.39	.29	.16															
0.50	.21	.39	.47	.51	.51	.48	.43	.35	.24	.09															
0.6	.21	.37	.43	.45	.42	.37	.28	.15																	
0.7	.20	.35	.39	.39	.34	.25	.12																		
0.8	.20	.33	.36	.33	.26	.13																			
0.9	.19	.31	.32	.27	.17	.01																			
1.0	.18	.29	.29	.22	.09																				
1.1	.18	.27	.25	.17	.01																				
1.2	.17	.25	.22	.11																					
1.3	.17	.24	.19	.06																					
1.4	.17	.22	.16	.01																					
1.5	.16	.21	.13																						
1.6	.16	.19	.11																						
1.7	.15	.18	.08																						
1.8	.15	.17	.05																						
1.9	.15	.15	.03																						
2.0	.14	.14																							
2.1	.14	.13																							
2.2	.13	.12																							

	k_a/k_L																								
$\frac{D_o}{L_o}$	5.1	5.3	5.5	5.7	5.9	6.1	6.3	6.5	6.7	6.9	7.1	7.3	7.5	7.7	7.9	8.1	8.3	8.5	8.7	8.9	9.1	9.3	9.5	9.7	9.9
0.00	2.03	2.06	2.08	2.11	2.14	2.16	2.19	2.21	2.24	2.26	2.28	2.30	2.32	2.35	2.37	2.39	2.41	2.43	2.44	2.46	2.48	2.50	2.52	2.53	2.55
0.02	1.92	1.94	1.97	1.99	2.01	2.03	2.05	2.07	2.09	2.11	2.13	2.15	2.16	2.18	2.20	2.21	2.23	2.24	2.26	2.27	2.28	2.30	2.31	2.32	2.33
0.04	1.80	1.82	1.84	1.86	1.87	1.89	1.90	1.92	1.93	1.94	1.96	1.97	1.98	1.99	2.00	2.01	2.01	2.02	2.03	2.03	2.04	2.05	2.05	2.06	2.06
0.06	1.68	1.69	1.70	1.71	1.72	1.73	1.73	1.74	1.74	1.75	1.75	1.75	1.75	1.75	1.75	1.75	1.75	1.75	1.74	1.74	1.73	1.73	1.72	1.71	1.70
0.08	1.53	1.54	1.54	1.54	1.54	1.54	1.53	1.53	1.52	1.51	1.50	1.49	1.48	1.46	1.45	1.43	1.41	1.39	1.36	1.34	1.31	1.28	1.24	1.21	1.17
0.10	1.37	1.36	1.35	1.34	1.33	1.31	1.29	1.27	1.24	1.22	1.19	1.15	1.11	1.07	1.03	.97	.92	.85	.78	.70	.62	.51	.40	.26	.09
0.12	1.18	1.16	1.13	1.10	1.07	1.03	.99	.94	.88	.82	.75	.67	.58	.47	.35	.21	.03								
0.14	.97	.92	.87	.81	.74	.67	.58	.48	.36	.21	.04														
0.16	.70	.62	.53	.42	.29	.14																			
0.18	.36	.22	.05																						

4. Compute k_a/k_L and D_o/L_o.

5. Using the ratios k_a/k_L and D_o/L_o, find D_c/L_o where D_c is the critical deficit.

6. Finally, calculate $D_c = (D_c/L_o)\, L_o$, and $C_{min} = C_s - D_c$.

To use Table IV-18 complete these steps:

1.-4. Repeat steps 1 through 3 above.

5. Using the ratios k_a/k_L and D_o/L_o, find $k_a t_c$.

6. Calculate $t_c = (k_a t_c)/k_a$.

4.3.8 General Dissolved Oxygen Deficit Equation

The most general dissolved oxygen mass-balance formulation to be presented in this chapter is as follows:

$$\begin{aligned} D = & \left(\frac{k_L}{k_a - k_L}\right)\left(L_o - \frac{L_{rd}}{k_L}\right)\left[\exp\left(\frac{-j_L}{A_o} f(x)\right) - \exp\left(\frac{-j_a}{A_o} f(x)\right)\right] \\ & + \left(\frac{k_N}{k_a - k_N}\right)\left(N_o - \frac{N_{rd}}{k_N}\right)\left[\exp\left(\frac{-j_N}{A_o} f(x)\right) - \exp\left(\frac{-j_a}{A_o} f(x)\right)\right] \\ & + \frac{R + S_B + L_{rd} + N_{rd} - P}{k_a}\left[1 - \exp\left(\frac{-j_a}{A_o} f(x)\right)\right] \\ & + D_o \exp\left(\frac{-j_a}{A_o} f(x)\right) \end{aligned} \tag{IV-49}$$

where

P = oxygen production rate due to photosynthesis, mg/l/day

R = oxygen utilization rate due to respiration, mg/l/day

S_B = benthic demand of oxygen, mg/l/day

The distance function f(x) expresses the cross-sectional area relationship throughout the reach. The area can increase or decrease linearly or remain constant. The general form of the relationship is:

$$f(x) = A_o x + \Delta_A\, x^2/_2 \;,\; \Delta_A = \frac{A_f - A_o}{x_L}$$

where

A_f = area at $x = x_L$

A_o = area at $x = 0$

x_L = length of reach

For a reach of constant cross-sectional area, $\Delta_A = 0$.

In developing Equation IV-49 the following relationship for CBOD was used (as originally presented in the BOD section):

$$L = \left(L_o - \frac{L_{rd}}{k_L}\right) \exp\left(\frac{-j_L}{A_o}\; f(x)\right) + \frac{L_{rd}}{k_L} \qquad \text{(IV-22)}$$

An analogous expression for NBOD was also used.

In Equation IV-49, the distributed sources and sinks (P, R, S_B, L_{rd}, N_{rd}) are all mass fluxes, and no volumetric flow rate is associated with any of these sources and sinks of dissolved oxygen.

4.3.9 Photosynthesis and Respiration

The difficulty of accurately assessing the impact of photosynthesis and respiration on the dissolved oxygen resources of streams is not readily apparent from the single terms appearing in Equation IV-49. Of concern are both free floating and attached algae, as well as aquatic plants. The extent to which algae impact the dissolved oxygen resources of a river is dependent on many factors, such as turbidity, which can decrease light transmittance through the water column. Additionally, the photosynthetic rate constantly changes in response to variations in sunlight intensity and is not truly constant as implied by Equation IV-49. Hence if algal activity is known to be a significant factor affecting the dissolved oxygen balance, the use of a computer model is recommended in order to accurately assess such influences. For example, in the Truckee River in California and Nevada, the diurnal variation of dissolved oxygen has exhibited a range of from 150 percent saturation during the daylight hours to 50 percent saturation at night due to algal photosynthesis and respiration, respectively. At the most, hand calculations can give estimates of net dissolved oxygen production rates that then can be compared to the other source/sink terms in Equation IV-28. From this comparison the significance of each can be estimated.

Table IV-19 presents some observed values of photosynthetic oxygen production rates. As shown in the table dissolved oxygen production is expressed in units of rate per unit area (gm/m -day). To convert to units of concentration per unit time, the algal production rate must be divided by river depth:

$$P = \frac{\overline{P}}{H} \tag{IV-50}$$

where

$\overline{P}$ = production rate of dissolved oxygen, gm/m^2-day
H = average river depth, meters
P = production rate of dissolved oxygen, mg/l-day

P can now be directly compared to other terms in Equation IV-28.

By using a regression equation developed by Erdmann (1979a, 1979b), the production rate of dissolved oxygen, P, can be determined directly if the diurnal variation of dissolved oxygen is known. When water temperature is fairly constant throughout the day, the photosynthetic oxygen production rate becomes

$$P = 2\Delta DO \tag{IV-51}$$

where

ΔDO = difference between the daily maximum dissolved oxygen concentration and the daily minimum dissolved oxygen concentration, mg/l

TABLE IV-19

SOME AVERAGE VALUES OF GROSS PHOTOSYNTHETIC PRODUCTION OF DISSOLVED OXYGEN (AFTER THOMANN, 1972 AND THOMAS AND O'CONNELL, 1966)

Water Type	Aver. Gross Production (grams/m^2-day)	Average Respiration (gm/m^2-day)
Truckee River - Bottom attached algae	9	11.4
Tidal Creek - Diatom Bloom (62-109.10^6 diatoms/l)	6	
Delaware Estuary - summer	3-7	
Duwamish River estuary - Seattle, Washington	0.5-2.0	
Neuse River System - North Carolina	0.3-2.4	
River Ivel	3.2-17.6	6.7-15.4
North Carolina Streams	9.8	21.5
Laboratory Streams	3.4-4.0	2.4-2.9

Since Equation IV-51 is based on regression analysis, the units are not consistent.

The importance of a constant water temperature is illustrated by Figure IV-20. This figure shows the hourly variation of dissolved oxygen over a 24

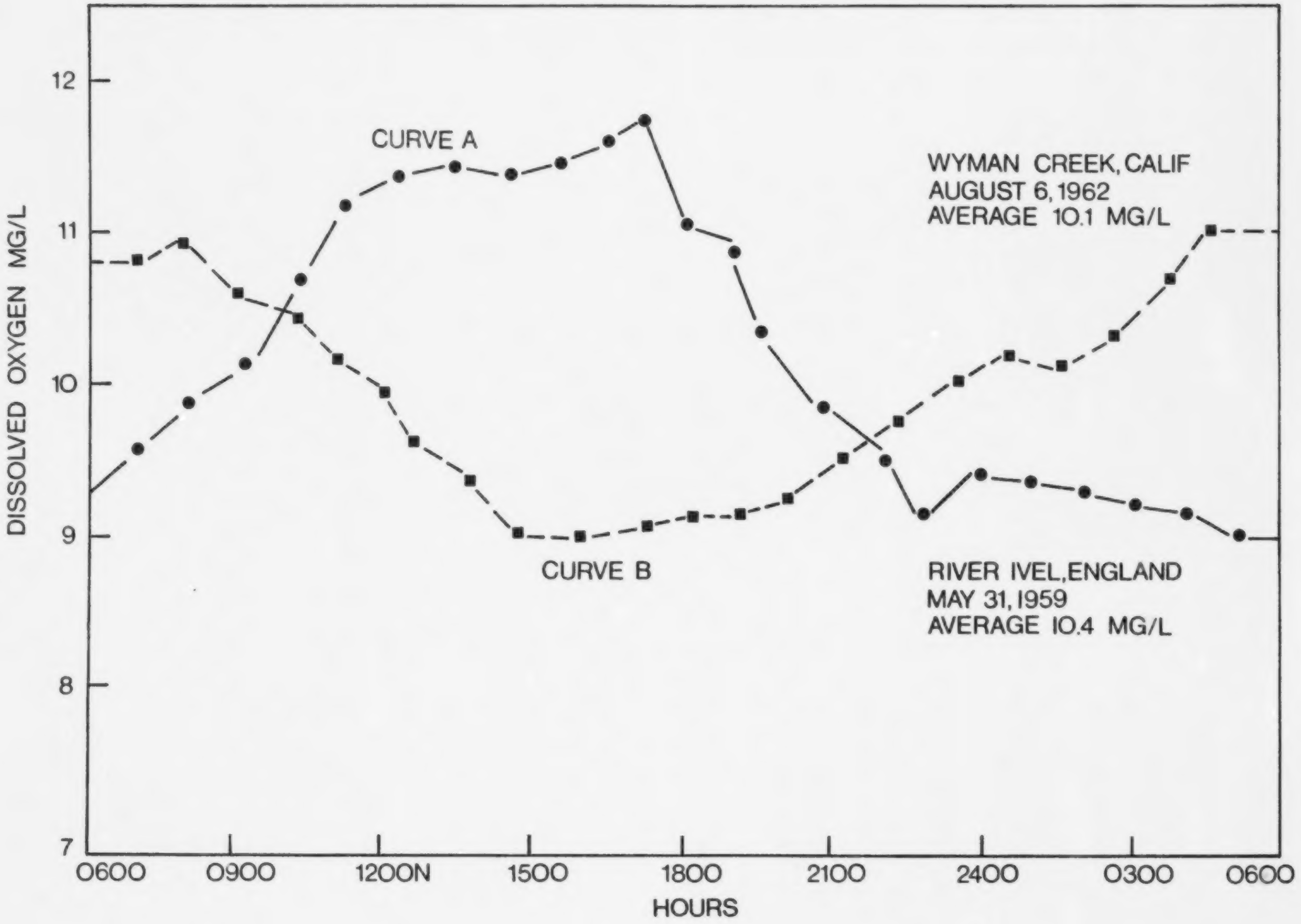


FIGURE IV-20 DAILY DISSOLVED OXYGEN VARIATION IN TWO RIVERS.

hour period for Wyman Creek in California and for the Ivel River in England. Both exhibit large diurnal dissolved oxygen variations, although the reasons differ. In curve A (Ivel River) the dissolved oxygen level gradually increases from 0600 hr to 1800 hr, and then decreases over the next 12 hours. The cause of the changing dissolved oxygen levels is a net photosynthetic oxygen production during the daylight hours, and a net comsumption during evening and night. Curve B is almost a mirror image of curve A since the minimum dissolved oxygen levels occur during daylight hours and the maximum during nighttime. The variations exhibited by curve B are principally caused by a changing water temperature. During the day this creek absorbs considerable solar radiation causing the water temperature to rise and the dissolved oxygen saturation level to decrease. At night the creek cools off and the dissolved oxygen saturation level increases. Curve B then is free from the influence of photosynthetic effects, so it would be erroneous to apply Equation IV-51. Erdmann (1979a, 1797b) and Kelly et al. (1975) provide more sophisticated methods to predict P when both photosynthetic and temperature effects occur concurrently. Example IV-7 illustrates the utility of Equation IV-51.

EXAMPLE IV-7

Prediction of Photosynthetic Oxygen Production Rate

On Mechums River near Charlottesville, Virginia, Kelly et al. (1975) collected the following data:

Time of Day (hours after midnight)	Stream Temperature, °C	Dissolved Oxygen (mg/ℓ)
0.0	23.3	7.6
0.5	23.3	7.6
1.0	23.4	7.6
1.5	23.4	7.5
2.0	23.5	7.4
2.5	23.5	7.2
3.0	23.5	7.3
3.5	23.5	7.3
4.0	23.4	7.3

Time of Day (hours after midnight)	Stream Temperature, °C	Dissolved Oxygen (mg/ℓ)
4.5	23.4	7.3
5.0	23.3	7.3
5.5	23.2	7.3
6.0	23.1	7.3
6.5	23.0	7.3
7.0	22.9	7.4
7.5	22.8	7.4
8.0	22.7	7.5
8.5	22.7	7.6
9.0	22.7	7.7
9.5	22.7	7.8
10.0	22.8	8.0
10.5	23.0	8.1
11.0	23.2	8.4
11.5	23.5	8.5
12.0	23.6	8.7
12.5	24.3	8.9
13.0	24.8	9.0
13.5	25.3	9.1
14.0	25.5	9.2
14.5	25.5	9.3
15.0	25.9	9.2
15.5	26.1	9.2
16.0	26.1	9.2
16.5	26.1	9.1
17.0	26.1	9.0
17.5	25.8	8.9
18.0	25.8	8.8
18.5	25.5	8.6
19.0	25.3	8.5
19.5	25.1	8.3
20.0	24.8	8.2
20.5	24.5	8.0
21.0	24.2	8.0
21.5	24.0	7.9
22.0	23.8	7.6
22.5	23.7	7.7
23.0	23.6	7.7
23.5	23.6	7.6
24.0	23.5	7.5

Using a sophisticated analysis, Kelly _et_ _al_. found the daily mean photosynthetic oxygen production to be 4.40 mg/l. Using the data shown above and Equation IV-51 estimate the daily photosynthetic oxygen production, P (mg/l/day).

The minimum dissolved oxygen is 7.2 mg/l, which occurs at 0230. The maximum dissolved oxygen is 9.3 mg/l which occurs at 1430. Hence:

$$P = 2\Delta DO = 2(9.3-7.2) = 4.2 \text{ mg/l/day}$$

This compares very well with the value found by Kelly et al. using a more sophisticated analysis, even though the stream temperature varies by a few degrees during the day. Probably one reason for the good agreement is that the maximum and minimum values occur about 12 hours apart, which the method assumes they do.

END OF EXAMPLE IV-7

Values of photosynthetic respiration vary widely, ranging from 0.5 gm/m^2/day to greater than 20 gm/m^2/day. One suggested relationship between respiration and chlorophyll a is given as (Thomann, 1972):

$$R(\text{mg/l/day}) = 0.024 \text{ (chlorophyll } \underline{a}) \; (\mu\text{g/l}) \qquad \text{(IV-52)}$$

where

$$1 \; \mu\text{g/l} = 10^{-3} \text{ mg/l}$$

Chlorophyl a concentration is most commonly expressed in terms of µg/l.

4.3.10 Benthic Demand

In addition to oxygen utilization by respiration of attached algae, benthic deposits of organic material and attached bacterial growth can utilize dissolved oxygen. Table IV-20 illustrates some uptake rates. As with photosynthesis, the uptake rates are expressed in gm/m^2-day. To use these values in Equations IV-28 or IV-49, division by stream depth (in meters) is necessary. Temperature effects can be approximated by

$$(S_B)_T = (S_B)_{20} \; 1.065^{T-20} \qquad \text{(IV-53)}$$

TABLE IV-20

AVERAGE VALUES OF OXYGEN UPTAKE RATES OF RIVER BOTTOMS (AFTER THOMANN, 1972)

Bottom Type and Location	Uptake (gms O_2/m^2-day) @ 20^oC	
	Range	Approximate Average
Sphaerotilus - (10 gm dry wt/M^2)	-	7
Municipal Sewage Sludge - Outfall Vicinity	2-10.0	4
Municipal Sewage Sludge - "Aged" Downstream of Outfall	1-2	1.5
Cellulosic Fiber Sludge	4-10	7
Estuarine mud	1-2	1.5
Sandy bottom	0.2-1.0	0.5
Mineral soils	0.05-0.1	0.07

The areal extent of significant oxygen demanding benthic materials is often limited to the region just below the outfall vicinity. Although the oxygen demand may be great over a short distance, it may be insignificant over larger distances. The response of rivers to areally limited benthic deposits is generally to move the critical deficit upstream, but not to lower its value significantly.

Zison et al (1978) contains significantly more data and further discussion of benthic oxygen demand in rivers. Additionally Butts and Evans (1978) conducted extensive studies of sediment oxygen demand on 20 streams in Illinois. They found that benthic oxygen demand could be predicted as:

$$\bar{S}_B = 0.15T + 0.3D_s + 0.11 \log N - 0.56 \qquad \text{(IV-54)}$$

where

$\bar{S}_B$ = benthic oxygen demand, g/m^2-day
T = water temperature, ^oC
D_s = depth of sediment, inches
N = number of macroinvertebrates per m^2

They found that N typically ranged from 10,000 to 1,000,000. Within this range the sum of the last two terms is between ±0.1, and is negligible compared to the first two terms. Under these conditions Equation IV-54 simplifies to

$$\bar{S}_B = 0.15T + 0.3D_s \qquad \text{(IV-55)}$$

The depths of sediment found during the study of Butts and Evans (1978) ranged from 1 to 17 inches. Consequently Equation IV-55 is applicable to streams which have fairly significant benthic oxygen demands. For cleaner streams Equation IV-55 probably overestimates the benthic oxygen demand.

4.3.11 Simplifying Procedures in Dissolved Oxygen Calculations

Using Equation IV-49 might be untenable for several reasons, such as lack of available data, or because of the voluminous calculations required to apply it to a large number of reaches. Several suggestions are offered here that should simplify analysis of dissolved oxygen problems.

Since the general scope of this section is to facilitate the determination of existing or potential problem areas, the analysis should proceed from the simple to the more complicated approach. It may be adequate to analyze the dissolved oxygen response to the most severe loadings first, neglecting those of secondary importance. If such an analysis clearly indicates dissolved oxygen problems, then the inclusion of any other pollutant discharges would only reinforce that conclusion. More rigorous procedures (e.g. a computer model) could then be employed to perform a detailed analysis.

Suppose the improvement of dissolved oxygen levels due to decreased loading from a point source is of interest. This is a common situation since it relates to the design of waste loading abatement schemes. Such improvement can be estimated by:

$$\Delta D = \Delta D_o \exp\left[\frac{-k_a x}{U}\right] + \left(\frac{k_L}{k_a - k_L}\right)\left(\Delta L_o\right)\left[\exp\left(\frac{-j_L}{A_o} f(x)\right) - \exp\left(\frac{-j_a}{A_o} f(x)\right)\right] \quad \text{(IV-56)}$$

where

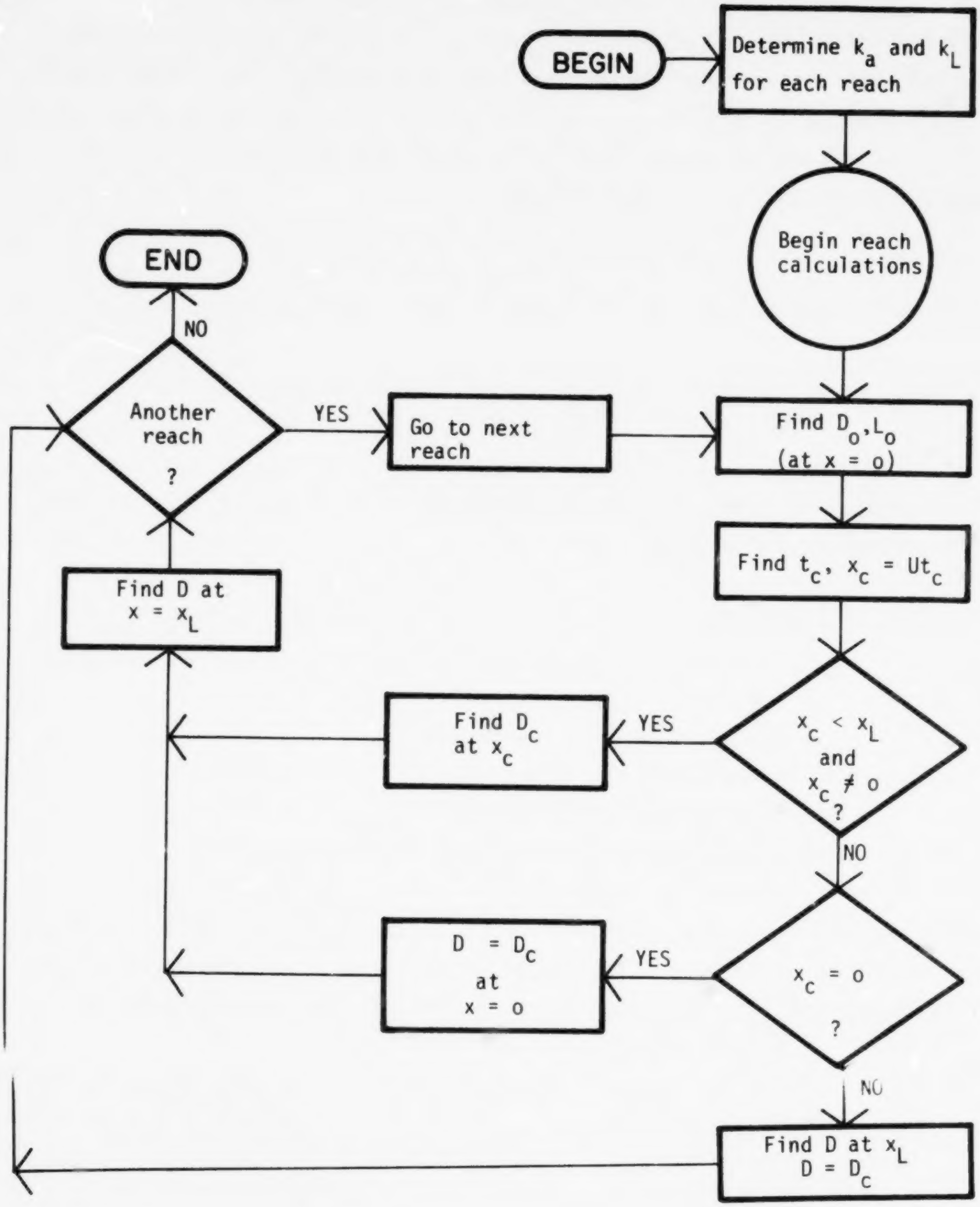
ΔL_o = the change in the initial BOD, mg/l

ΔD = change in deficit in response to ΔL_o

Equation IV-56 was formulated from Equation IV-49 assuming that L_o and D_o are the only changes of significance.

Many rivers have a large number of point sources. Although this is not necessarily a complicating factor, a detailed analysis might be too time consuming for hand calculations. There are several possible alternatives to deal with this situation in order to reduce the number of reaches to be analyzed. The first, already mentioned, is to consider only the significant pollutant sources. Second, as was illustrated in Example IV-5, a number of uniformly distributed point sources can be considered as a single distributed source. Third, combining several adjacent point sources is also possible, if the length of the reach under consideration is long relative to the distance of separation between the point sources. Analogously, a distributed source can be approximated as a point source, contributing the same waste loading and located at the center of the distributed source.

It may be that the planner wants only to determine the critical dissolved oxygen concentration in each of a series of reaches. In this case no more than two values of dissolved oxygen per reach need be calculated. Figure IV-21 shows the solution process to be followed.



BEGIN
Determine k_a and k_L for each reach
Begin reach calculations
Find D_o, L_o (at $x = o$)
Find t_c, $x_c = Ut_c$
$x_c < x_L$ and $x_c \neq o$?
YES
Find D_c at x_c
NO
$x_c = o$?
YES
$D = D_c$ at $x = o$
NO
Find D at x_L $D = D_c$
Find D at $x = x_L$
Another reach ?
YES
Go to next reach
NO
END

FIGURE IV-21 FLOW PROCESS IN REACH BY REACH SOLUTION TO CRITICAL DISSOLVED OXYGEN VALUES

One final note on dissolved oxygen evaluations should be made here. It may be that if the planner is interested primarily in locating dissolved oxygen problems, he need not perform any computations. This is especially likely where dissolved oxygen data are available at various locations on the river. Plotting dissolved oxygen time trends may reveal when, as well as where, annual dissolved oxygen minima occur.

EXAMPLE IV-8

Determining River Assimilative Capacity from Tables IV-17 and IV-18

Suppose the user wants to determine waste assimilative capacity (WAC) for a river reach that has the following characteristics:

critical dissolved oxygen concentration = 5.0 mg/l
(user establishes this)
initial deficit = 1.0 mg/l
average velocity = 0.5 fps
average depth = 4 feet
chloride concentration = 0
temperature range = 10^{o}C to 35^{o}C

First, k_a and k_L need to be found. From Figure IV-17, k_a (20^{o}) = 0.8/day, and from Figure IV-11, k_L = 0.4/day. At any other temperature then, $k_a$and k_L can be found from the temperature relationships previously developed:

$$k_a = (k_a)_{20} \; 1.024^{T-20} \qquad \text{(IV-34)}$$

$$k_L = (k_L)_{20} \; 1.047^{T-20} \qquad \text{(IV-17)}$$

Using Table IV-15 the dissolved oxygen saturation concentration within the temperature range of interest can be found. This information can be then compiled into Table IV-21 shown below.

TABLE IV-21

COMPILATION OF INFORMATION IN EXAMPLE IV-8

T (^oC)	C_s (mg/l)	C_c (mg/l)	D_c (mg/l)	D_o/D_c	k_a/k_L
10	11.3	5.0	6.3	0.16	2.5
15	10.2	5.0	5.2	0.19	2.2
20	9.2	5.0	4.2	0.24	2.0
25	8.4	5.0	3.4	0.29	1.8
30	7.6	5.0	2.6	0.38	1.6
35	7.1	5.0	2.1	0.48	1.4

Using the values of D_o/D_c and k_a/k_L, L_o can be found, which in this case is the WAC.

Procedure

1. Table IV-21 is entered at the appropriate k_a/k_L column. This is 2.5 at 10°C.

2. Next, the entry within the k_a/k_L column in Table IV-17 is found such that

$$\frac{D_o/L_o}{D_c/L_o} = \frac{D_o}{D_c} = 0.16$$

Since the left-most column of Table IV-17 is D_o/L_o and the entries are D_c/L_o, the ratio of these values is calculated until that ratio equals 0.16.

For example, try $D_o/L_o = 0.05$. Then $D_c/L_o = 0.23$ and

$$\frac{0.05}{0.23} = 0.22 > 0.16\text{, too big}$$

try $D_o/L_o = 0.04$. Then $D_c/L_o = 0.23$ and

$$\frac{0.04}{0.23} = .17\text{, close enough}$$

$$\text{then } \frac{D_c}{L_o} = .23\text{, or } L_o = \frac{6.3}{.23} = \underline{\underline{27.4}} \text{ mg/l}$$

The results are tabulated below for the temperature range 10°C to 35°C.

$T(^\circ C)$	WAC (mg/l)	D_o/L_o
10	27.4	0.04
15	20.0	0.05
20	15.0	0.07
25	11.3	0.09
30	7.6	0.13
35	5.4	0.19

L_o is directly related to the loading rate of BOD, as expressed earlier in Equation IV-41:

$$\text{WAC} = (L_o)_{\text{critical}} = \frac{L_u Q_u + W_{\text{critical}}/5.38}{Q_u + Q_w}$$

From equation IV-41 the critical waste loading W can be found. If desired, this procedure can be repeated for different river flow rates, and WAC and W_{critical} found for the various flows. To do this, different average depths and velocities will be needed. Generally this analysis is most applicable to minimum flow conditions, as this is the most critical situation, but higher flows may be of interest to assess the benefits of flow augmentation decisions. Novotny and

Krenkel (1975) have used a 20 year, 3-day low flow in analyzing the Holston River in Tennessee. For further discussion of low flow calculations refer to Section 4.4.6.

In interpreting the results of this example the user should be looking more at trends rather than particular results. For example, notice how the WAC decreases with increasing temperature. For every 10° increase the WAC is approximately halved. A similar relationship between WAC and flow rate could also be determined.

Finally, using Table IV-18, the travel time t_c can be determined to the point of critical deficit. The appropriate D_o/L_o and k_a/k_L values are used to find t_c. Table IV-22 illustrates these results.

TABLE IV-22

CRITICAL TRAVEL TIME RESULTS

$T(^oC)$	k_a/k_L	D_o/L_o	$t_c k_a$	k_a	t_c(days)
10	2.5	0.04	1.4	.63	2.2
15	2.2	.05	1.3	.71	1.8
20	2.0	.07	1.2	.8	1.5
25	1.8	.09	1.13	.9	1.2
30	1.6	.13	1.0	1.0	1.0
35	1.4	.19	0.9	1.1	0.8

END OF EXAMPLE IV-8

EXAMPLE IV-9

Critical Deficit Calculations for Multiple Reaches

Suppose the critical deficit in each of the three reaches of the river illustrated in Figure IV-22 is to be determined. The conditions upstream of the first discharge are:

$T = 27^{o}C$ depth = 5.0 feet

$Q = 600$ cfs $D_u = 1$ mg/l

$U = 0.4$ fps $L_u = 2$ mg/l

Using these data, along with the solution process outlined in Figure IV-21, the following procedure can be used:

1. Determine k_a, k_L for each reach. For this example it will be assumed that the average depth, velocity, and temperature remain relatively constant over the three reaches, so that k_a and k_L are also the same.

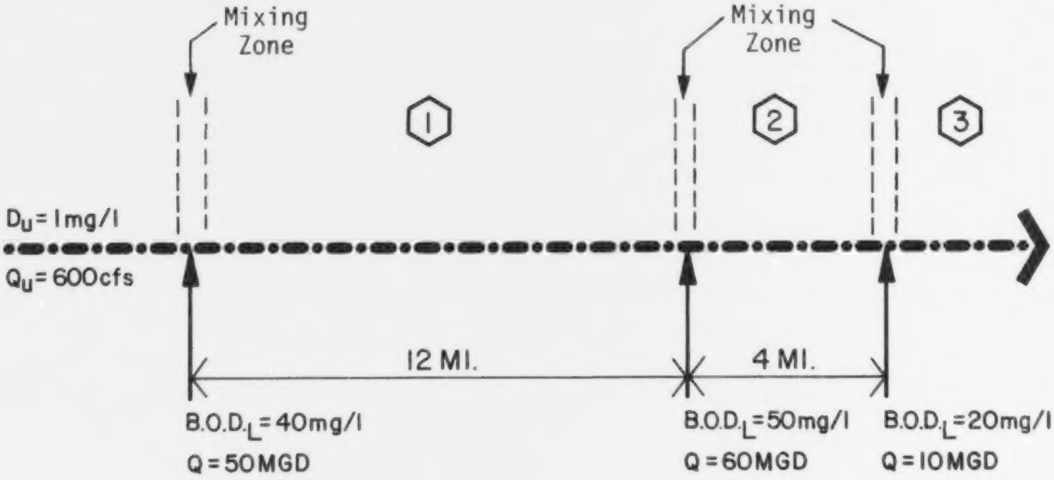

Mixing Zone
Mixing Zone
1
2
3
D_u = 1mg/l
Q_u = 600cfs
12 MI.
4 MI.
B.O.D._L = 40mg/l
Q = 50MGD
B.O.D._L = 50mg/l
Q = 60MGD
B.O.D._L = 20mg/l
Q = 10MGD

FIGURE IV-22 HYPOTHETICAL RIVER USED IN EXAMPLE IV-9

k_a (20) = 0.5, (from Figure IV-17)

k_L (20) = 0.35, (from Figure IV-11)

Using the temperature correction:

k_a (27) = 0.60, (from Equation IV-34)

k_L (27) = 0.48, (from Equation IV-17)

The saturation dissolved oxygen concentration at 27°C and 0‰ salinity is (from Table IV-15) 8.1 mg/l.

2. For the first reach, calculate L_o and D_o.

$$L_o = \frac{(2)(600)+(40)\ (50)\ (1.55)}{600+(50)(1.55)} = 6.35 \text{ mg/l}$$

For lack of better information about the dissolved oxygen characteristics of the waste, it can be assumed that $D_o = D_u = 1$ mg/l. The location of the critical deficit can now be calculated using Table IV-18, or Equation IV-45. In this example Table IV-18 will be used. To use that table, the following ratios are needed:

$$D_o/L_o = 1/6.35 = 0.16$$

and

$$k_a/k_L = 0.60/0.48 = 1.3$$

From Table IV-18, $k_a t_c$ = .92 or

$$t_c = .92/0.6 = 1.53 \text{ days}$$

$$x_c = \frac{(0.4)\ (1.53)\ (3600)\ (24)}{5280} = 10.0 \text{ miles}$$

Since $x_c < 12$, the critical deficit actually exists, and is located 10 miles downstream. From Table IV-17 D_c can be found by entering it with the same ratios used in Table IV-18. The result is:

$$\frac{D_c}{L_o} = .38 \rightarrow D_c = \underline{\underline{2.4}} \text{ mg/l}$$

3. Before the critical conditions in reach 2 can be calculated, the conditions at the upstream end of that reach must be established. The conditions at the downstream end of reach 1 are

$D = 2.3$ mg/l, from Equation IV-40
$L = 2.6$ mg/l from Equation IV-42

The conditions at the upstream end of reach 2 are thus:

$$L_o = \frac{(2.6)\ (677)+(60)\ (1.55)}{677 + 93} = 8.35 \text{ mg/l}$$

$D_o = 2.3$ can be used for lack of better information on the dissolved oxygen concentration in the effluent to reach 2. For use in Table IV-18, it is found that

$$D_o/L_o = .28$$

So

$k_a t = .76$
$t_c = .76/0.6 = 1.3$ days
$x_c = 8.3$ miles

Since reach 2 is only 4.0 miles long, the critical deficit is not reached. Instead the maximum deficit will occur at the downstream end of reach 2, where:

$\underline{D = 3.3\ mg/l}$, Equation IV-40

$\underline{L = 6.22\ mg/l}$, Equation IV-22

4. For the beginning of reach 3, L_o and D_o must be found.

$$L_o = \frac{(20)(10)(1.55) + (770.5)\ (6.22)}{770.5 + (10)(1.55)} = 6.5\ mg/l$$

For D_o, it can be assumed that C_w = 5.0 mg/l. From Equation IV-41, then

$$D_o = 8.1 - \frac{(8.1 - 3.3)\ (770.5) + (5.0)(10)\ (1.55)}{770.5 + 15.5} = 3.3\ mg/l$$

The calculations of critical conditions can now be made for this reach, as for the previous two.

END OF EXAMPLE IV-9

4.4 TEMPERATURE

4.4.1 Introduction

The biota comprising an established aquatic ecosystem generally respond negatively to significant abnormal temperature fluctuations. Anthropogenic modifications of rivers and streams can alter the thermal regime, most often by elevating the maximum and mean water temperatures. Repercussions of elevated temperatures are manifested through a shift in the ecological balance and in the water quality of rivers. For example, there is a progression in the predominance of algal species from diatoms to green algae to blue-green algae as water temperature increases through a specific range. Thermal discharges can increase the ambient temperature enough to alter the predominant species to the undesirable blue-green algae. Increased metabolic activity of aquatic organisms, such as fish, also accompanies elevated temperature. If the increase is high enough, the results can be lethal. Much data are available today (e.g., Committee on Water Quality Criteria, 1972) which specify lethal threshold temperatures for aquatic organisms.

Water quality may be adversely affected through decreased solubility of dissolved oxygen and increased biochemical reaction rates. Adequate dissolved oxygen levels, particularly at elevated temperatures, are critical because of the increased metabolic activity. Yet, as previously discussed the saturation concentration of dissolved oxygen diminishes with rising temperature. Worse still, is the concurrent low flow condition which is associated, in many parts of the country, with the warm summer months. For example, in a study of 30 river reaches in the U.S. (EPA, 1974), 20 had lower flows in the summer months than in the winter. This situation further reduces assimilative capacity and usually results in the most critical dissolved oxygen levels over the year.

Man can alter the thermal regime of rivers by removing trees, changing the flow regime, and by increasing thermal discharges. Diversions of water from a river can reduce the water depth, and increase the mean and diurnal fluctuation of stream temperature.

In Long Island, modification of the natural environment of streams has increased average stream temperatures during the summertime by as much as 9 to 14^{O}F (Pluhowski, 1968). Concurrent temperature differences of as much as 14 to 18^{O}F between sites on the same stream were observed on days of high solar radiation. A principal factor involved in these occurrences was the removal of vegetation along the banks of the streams, permitting significantly greater penetration of solar radiation. Other contributing factors cited by Pluhowski included increased stormwater runoff, a reduction in the amount of groundwater inflow, and the introduction of ponds and lakes.

4.4.2 Equilibrium Temperature

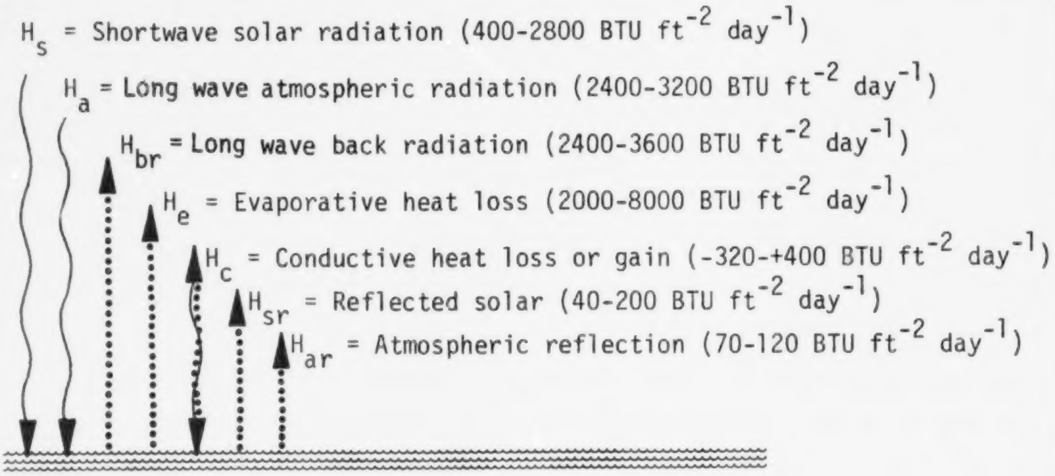
If a body of water at a given initial temperature is exposed to a set of constant meteorological conditions, it will tend to approach some other temperature asymptotically. It may warm by gaining heat or cool by losing heat. Theoretically, after a long period of time the temperature will become constant and the net heat transfer will be zero. This final temperature has been called the equilibrium temperature, E. At equilibrium, the heat gained by absorbing solar radiation and long-wave radiation from the atmosphere will exactly balance the heat lost by back radiation, evaporation, and conduction.

These heat fluxes are illustrated in Figure IV-23 which also shows typical ranges for the fluxes. Some of these terms (H_s,H_a,H_{sr}, H_{ar}) are independent of water temperature, while the remainder (H_{br},H_c,H_e) are dependent upon water temperature. At equilibrium then, H_n (net transfer) equals zero, or

$$H_s - H_{sr} + H_a - H_{ar} - H_{br} - H_c - H_e = 0 \qquad \text{(IV-57)}$$

In actuality, the water temperature rarely equals the equilibrium temperature because the equilibrium temperature itself is constantly changing with the local meteorological conditions. The equilibrium temperature will rise during the day when solar radiation is greatest, and fall to a minimum at night when solar radiation is absent.

A daily average equilibrium temperature may be computed using a number of factors including daily average values of radiation, temperature, wind speed, and vapor pressure. The daily average value will reach a maximum in midsummer and a minimum in midwinter. Since the actual water temperature always tends to approach, but does not reach the equilibrium temperature, it will usually be less than equilibrium


H_s = Shortwave solar radiation (400-2800 BTU ft^{-2} day^{-1})
H_a = Long wave atmospheric radiation (2400-3200 BTU ft^{-2} day^{-1})
H_{br} = Long wave back radiation (2400-3600 BTU ft^{-2} day^{-1})
H_e = Evaporative heat loss (2000-8000 BTU ft^{-2} day^{-1})
H_c = Conductive heat loss or gain (-320-+400 BTU ft^{-2} day^{-1})
H_{sr} = Reflected solar (40-200 BTU ft^{-2} day^{-1})
H_{ar} = Atmospheric reflection (70-120 BTU ft^{-2} day^{-1})

NET RATE AT WHICH HEAT CROSSES WATER SURFACE

$$H_n = \left[\underbrace{(H_s + H_a - H_{sr} - Har)} \quad - \quad \underbrace{(H_{br} \pm H_c + H_e)}\right] \text{BTU ft}^{-2} \text{ day}^{-1}$$

Absorbed Radiation (H_R)
Independent of Water Temperature

Temperature Dependent Terms

$$H_{br} \sim (T_s + 460)^4$$

$$H_c \sim (T_s - T_a)$$

$$H_e \sim W(e_s - e_a)$$

FIGURE IV-23 MECHANISMS OF HEAT TRANSFER ACROSS A WATER SURFACE (PARKER AND KRENKEL, 1969)

in the spring when temperatures are rising, and greater than equilibrium in the fall when temperatures are dropping. During a 24 hour period, the equilibrium temperature usually rises above the actual water temperature during the day and falls below the water temperature at night, forcing the water temperature to follow a diurnal cycle.

The amplitude of the actual diurnal water temperature cycle is generally dampened significantly in comparison to the amplitude of the equilibrium temperature cycle due to the large heat capacity of water. A thermal discharge into a water body will usually increase the actual daily amplitude because of the water temperature dependent terms in Equation IV-57. This situation is illustrated in the following example (Edinger, et al., 1968). Figure IV-24 illustrates a flow through cooling pond into which a thermal effluent is discharged (at Station B).

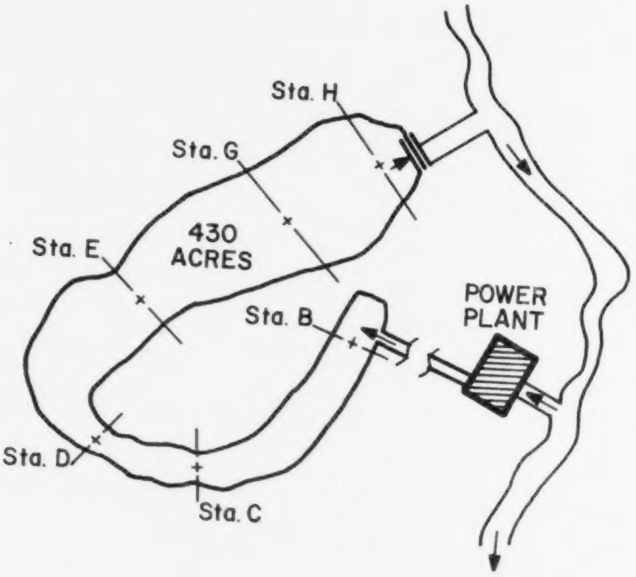


FIGURE IV-24 SCHEMATIC OF SITE NO. 3 COOLING LAKE (FROM EDINGER, ET AL., 1968)

Temperature observations were recorded at Stations B through H at four-hour periods for one week. The findings are depicted in Figure IV-25.

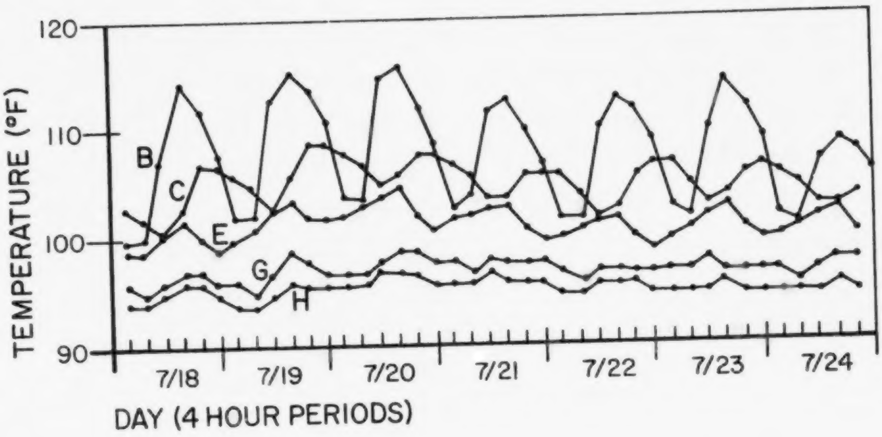


FIGURE IV-25 OBSERVED TEMPERATURES, SITE NO. 3, JULY 18 - JULY 24, 1965 (EDINGER, ET AL., 1968)

The highest temperatures and largest diurnal temperature variables are recorded at Station B. The peak temperature at Station B occurs just after noon, corresponding to the peak loading from the plant. At Station C the peak temperature is at 1800 hours, indicating the lag in flow time from Stations B to C. The peak temperatures at the remaining stations are more influenced by meteorological conditions, and less by the thermal discharge. The relationship of the observed temperatures to the equilibrium temperature over a 24-hour period is shown in Figure IV-26. Note the amplitude of the equilibrium temperature E (33^{O}F amplitude). The average equilibrium temperature, $\overline{E}$, is approximately 91^{O}F. A progression from Station B to Station H indicates that the daily water temperature tends to approach the average equilibrium temperature.

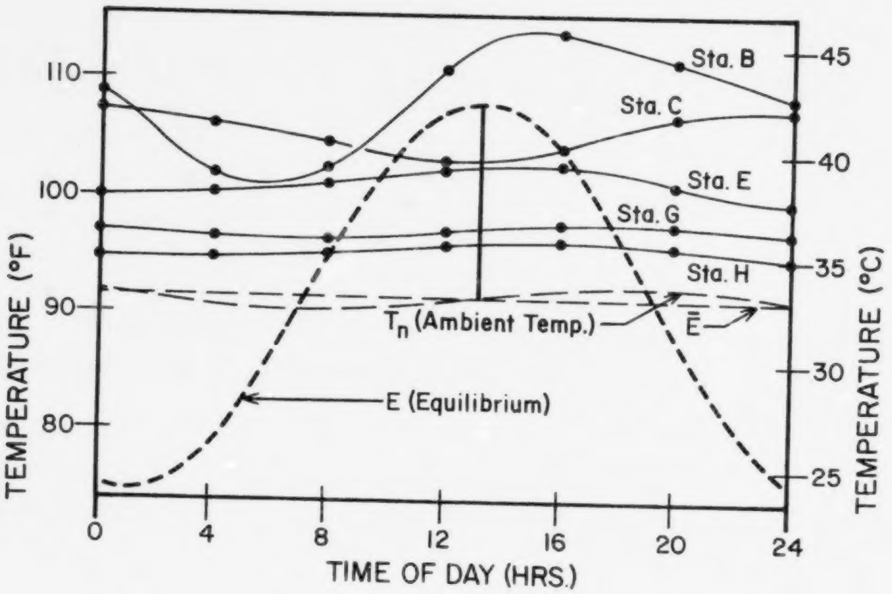


FIGURE IV-26 COMPARISON OF COMPUTED EQUILIBRIUM AND AMBIENT TEMPERATURES WITH OBSERVED MEAN DIURNAL TEMPERATURE VARIATIONS FOR SITE NO. 3, JULY 18-JULY 24, 1966 (EDINGER, ET AL., 1968)

Stations G and H, and the ambient temperature T_N, all reflect the predominating influence of meteorological conditions. When the ambient water temperature is above the instantaneous equilibrium temperature E, it tends to decrease, and when the temperature is below E, it tends to increase. In the early morning and late evening hours, when E is low, the water temperature decreases at these stations. During midday when E is higher, however, the temperatures at these stations increase.

4.4.3 Calculation of Equilibrium Temperature

Studies (Edinger and Geyer, 1965) have shown that the equilibrium temperature of a well mixed body of water can be estimated by:

$$E = -\frac{0.05E^2}{K} + \frac{H_R - 1801}{K} + \frac{K - 15.7}{K\,(.26+B)} \left[e_a - C(B) + 0.26T_a\right] \quad \text{(IV-58)}$$

where

E = equilibrium temperature, °F

K = thermal exchange coefficient, BTU/ ft^2/day/°F

H_R = net incoming short (H_{sn}) and long (H_{an}) wave radiation BTU/ft^2/day

T_a = air temperature, °F

e_a = water vapor pressure of ambient air at air temperature, mmHg

B = proportionality coefficient, mmHg/°F

$C(B)$ = value dependent on B, mmHg

The thermal exchange coefficient K is expressible as:

$$K = 15.7 + (0.26+B)\ f(u) \quad \text{(IV-59)}$$

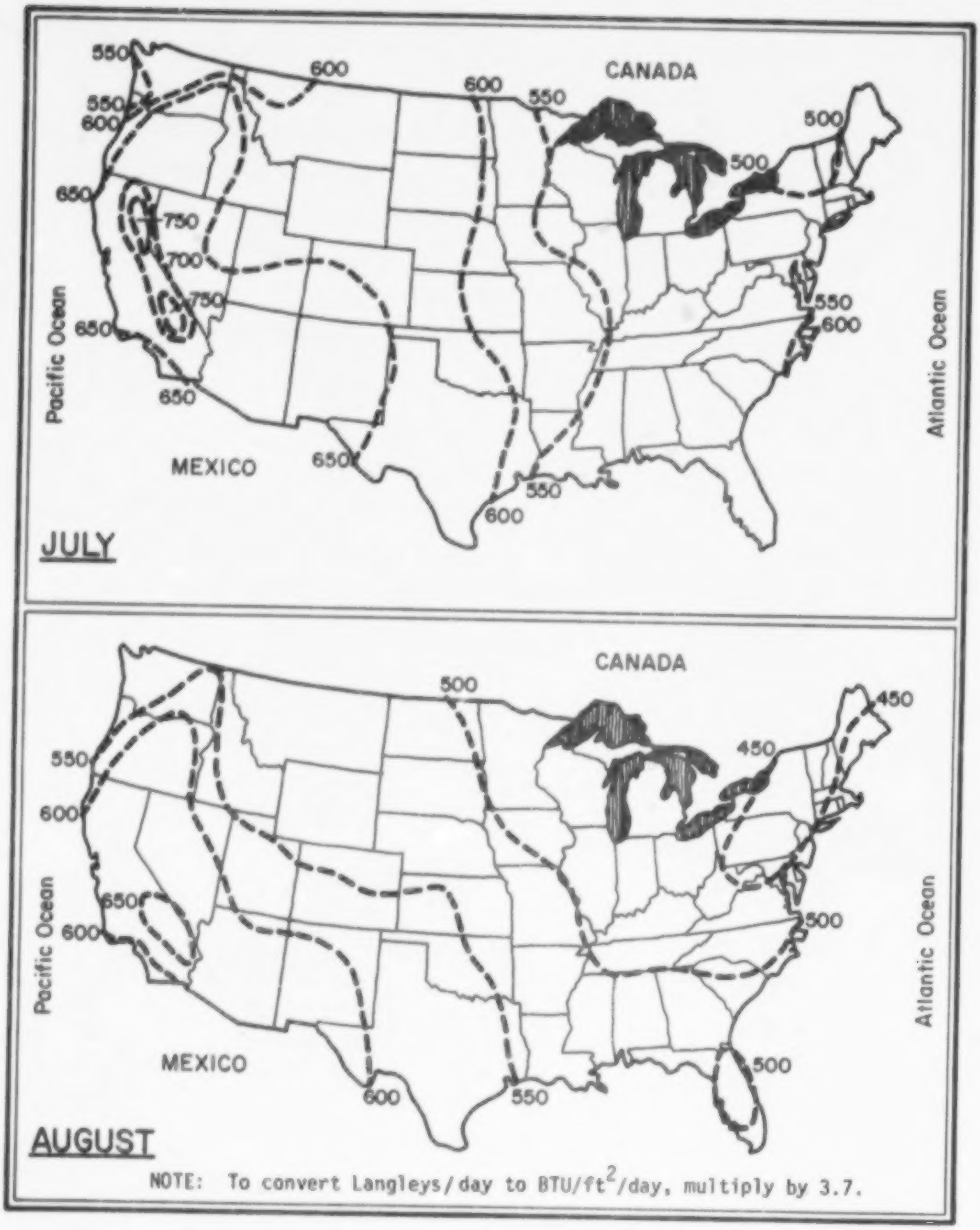
where f(u) is a function of wind speed. Different relationships for f(u) have been developed. For purposes of hand calculations, the following relationship will be used:

$$f(u) = 11.4u \quad \text{(IV-60)}$$

where u is the daily average wind speed in mph.

To calculate E using Equation IV-58 an iterative procedure is needed, since K, B, and C(B) depend on E. The following steps outline a solution procedure.

1. Data needed to start the procedure include: T_a, relative humidity, wind speed, and net shortwave solar radiation. Figure IV-27 illustrates daily average solar radiation reaching the continental United States


CANADA
550
550
600
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600
550
500
500
650
750
700
750
650
650
550
600
Pacific Ocean
Atlantic Ocean
MEXICO
650
550
600
JULY
CANADA
500
450
450
550
600
650
600
500
Pacific Ocean
Atlantic Ocean
MEXICO
500
600
550
AUGUST

NOTE: To convert Langleys/day to BTU/ft^2/day, multiply by 3.7.

Figure IV-27 Mean Daily Solar Radiation (Langleys) throughout the U.S. for July and August (U.S. Department of Commerce, 1968)

for the months July and August. It is during these months that stream temperatures usually reach their annual maxima. These values do not account for the albedo of water (the percent of incoming solar radiation that is reflected), but since this is small, it can be ignored. Because of the variability caused by topography, vegetative cover, and other factors, local sources of information should be used when possible for solar radiation values.

2. Calculate $H_R = H_{sn} + H_{an}$ (BTU/ ft^2/day). If Figure IV-27 is utilized for H_{sn}, convert from langleys/day to BTU/ft^2/day by multiplying by 3.7. H_{an} can be estimated from Table IV-23 by knowing the air temperature and the cloud cover fraction (0.1 to 1.0).

3. Determine e_a from Table IV-24 by entering with T_a and relative humidity.

4. Choose an initial value for E. The air temperature T_a can be the first guess.

5. Enter Table IV-25 for B and C(B) at E (^oF).

6. Knowing u, f(u), and B, calculate K from Equation IV-59.

7. From Equation IV-58 make the next estimate of E (E_{new}) by evaluating the right hand side of that equation (call this result F(E)).

TABLE IV-23

NET LONG WAVE ATMOSPHERIC RADIATION, H_{an}

Cloud Cover	Temperature (^oF)	H_{an} (BTU/Sq. Ft/Day)	Temperature (^oF)	H_{an} (BTU/Sq. Ft/Day)	Temperature (^oF)	H_{an} (BTU/Sq. Ft/Day)	Temperature (^oF)	H_{an} (BTU/Sq. Ft/Day)	Temperature (^oF)	H_{an} (BTU/Sq. Ft/Day)	Temperature (^oF)	H_{an} (BTU/Sq. Ft/Day)
.1	35	1685	40	1790	45	1900	50	2016	55	2138	60	2266
	65	2400	70	2540	75	2688	80	2842	85	3004	90	3173
.2	35	1694	40	1799	45	1910	50	2026	55	2149	60	2277
	65	2412	70	2553	75	2701	80	2857	85	3019	90	3190
.3	35	1708	40	1814	45	1926	50	2043	55	2167	60	2296
	65	2432	70	2575	75	2724	80	2881	85	3045	90	3216
.4	35	1728	40	1335	45	1949	50	2067	55	2192	60	2323
	65	2461	70	2605	75	2756	80	2914	85	3080	90	3254
.5	35	1754	40	1863	45	1978	50	2098	55	2225	60	2358
	65	2497	70	2644	75	2797	80	2958	85	3126	90	3303
.6	35	1785	40	1896	45	2013	50	2136	55	2265	60	2400
	65	2542	70	2691	75	2847	80	3011	85	3182	90	3362
.7	35	1822	40	1936	45	2055	50	2180	55	2312	60	2450
	65	2595	70	2747	75	2907	80	3074	85	3249	90	3432
.8	35	1865	40	1981	45	2103	50	2232	55	2366	60	2508
	65	2656	70	2812	75	2975	80	3146	85	3325	90	3513
.9	35	1914	40	2033	45	2158	50	2290	55	2428	60	2573
	65	2725	70	2885	75	3053	80	3228	85	3412	90	3604
1.0	35	1968	40	2091	45	2220	50	2355	55	2497	60	2646
	65	2803	70	2967	75	3139	80	3320	85	3509	90	3707

TABLE IV-24

WATER VAPOR PRESSURE (mmHg) VERSUS AIR TEMPERATURE, T_a, AND RELATIVE HUMIDITY

T_a	e_s*	RELATIVE HUMIDITY									
(°F)	(mmHg)	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
35	5.2	0.5	1.0	1.6	2.1	2.6	3.1	3.6	4.2	4.7	5.2
40	6.3	0.6	1.3	1.9	2.5	3.2	3.8	4.4	5.0	5.7	6.3
45	7.6	0.8	1.5	2.3	3.0	3.8	4.6	5.3	6.1	6.8	7.6
50	9.1	0.9	1.8	2.7	3.6	4.6	5.5	6.4	7.3	8.2	9.1
55	11.0	1.1	2.2	3.3	4.4	5.5	6.6	7.7	8.8	9.9	11.0
60	13.1	1.3	2.6	3.9	5.2	6.6	7.9	9.2	10.5	11.8	13.1
65	15.6	1.6	3.1	4.7	6.2	7.8	9.4	10.9	12.5	14.0	15.6
70	18.6	1.9	3.7	5.6	7.4	9.3	11.2	13.0	14.9	16.7	18.6
75	22.0	2.2	4.4	6.6	8.8	11.0	13.2	15.4	17.6	19.8	22.0
80	26.0	2.6	5.2	7.8	10.4	13.0	15.6	18.2	20.8	23.4	26.0
85	30.5	3.1	6.1	9.2	12.2	15.3	18.3	21.4	24.4	27.5	30.5
90	35.8	3.6	7.2	10.7	14.3	17.9	21.5	25.1	28.6	32.2	35.8
95	41.8	4.2	8.4	12.5	16.7	20.9	25.1	29.3	33.4	37.6	41.8
100	48.7	4.9	9.7	14.6	19.5	24.4	29.2	34.1	39.0	43.8	48.7

* e_s = saturated vapor pressure

TABLE IV-25

B AND C(B) AS FUNCTIONS OF TEMPERATURE

Temperature (°F)	B (mmHg/°F)	C(B) (mmHg)	Temperature (°F)	B (mmHg/°F)	C(B) (mmHg)
45	.286	-5.5	70	.660	-22.9
46	.296	-4.5	71	.680	-23.6
47	.306	-4.1	72	.701	-24.4
48	.317	-4.2	73	.722	-25.4
49	.328	-4.6	74	.743	-26.5
50	.340	-5.4	75	.765	-27.8
51	.352	-6.3	76	.787	-29.3
52	.365	-7.5	77	.810	-31.0
53	.378	-8.7	78	.833	-33.0
54	.391	-10.0	79	.857	-35.1
55	.405	-11.2	80	.881	-37.6
56	.419	-12.5	81	.905	-40.3
57	.433	-13.6	82	.930	-43.2
58	.448	-14.7	83	.955	-46.4
59	.464	-15.8	84	.980	-49.7
60	.479	-16.7	85	1.006	-53.3
61	.496	-17.6	86	1.033	-57.1
62	.512	-18.3	87	1.060	-61.0
63	.529	-19.0	88	1.087	-64.9
64	.547	-19.6	89	1.114	-68.9
65	.564	-20.1	90	1.142	-72.9
66	.583	-20.7	91	1.171	-76.7
67	.601	-21.2	92	1.200	-80.4
68	.620	-21.7	93	1.229	-83.8
69	.640	-22.3	94	1.259	-86.8
			95	1.289	-89.3

8. The next estimate of E is:

$$E_{new} = 0.3E + 0.7\ F(E)$$

(Note: this choice of E_{new} brings about a more rapid convergence to the answer than would use of E alone).

9. If $|E_{new} - E| \leq 1^{o}F$, then $E_{actual} = E_{new}$.
If $|E_{new} - E| > 1^{o}F$, return to step 5 with E_{new} and repeat the procedure until the convergence criterion is met, namely, $E_{actual} = E_{new}$.

Instantaneous, daily average, weekly average, or even longer term average equilibrium temperature, $\overline{E}$, can be calculated by using mean meteorological conditions over the period of interest and following the solution procedure just outlined. Calculating the daily average $\overline{E}$ under the most crucial annual meteorological conditions (usually occurring in July or August) yields the highest temperature about which that water body tends to naturally oscillate. The repercussions of man's activities in terms of altering $\overline{E}$ can thus be estimated and analyzed for potential impact.

EXAMPLE IV-10

Calculation of Equilibrium Temperature

On Long Island, New York, studies done by Pluhowski (1968) have indicated that shading of streams by a natural vegetative canopy can drastically affect the shortwave solar radiation reaching those streams. The results of some of his findings are presented in Table IV-26. In the summer, when leaves are on the trees, the actual solar radiation reaching the Connetquot River can be as low as 29% of that reaching unobstructed sites at nearby Mineola or Brookhaven.

TABLE IV-26

SUMMARY OF SOLAR-RADIATION DATA FOR MINEOLA, BROOKHAVEN, AND THE CONNETQUOT RIVER SITES

		Mean-Daily Solar Radiation in Langleys: for the Indicated Periods				Ratio= Connetquot River Observed / Connetquot River Unobstructed
Solar Site (1)	Dates (2)	Mineola (3)	Brookhaven (4)	Connetquot River Estimated (5)	Connetquot River Observed (6)	(7)
1	Jan. 30, 31, 1967	235	244	240	148	0.62
2	Jan. 28, 29, 1967	148	130	137	96	.70
3	Jan. 25, 26, 1967	135	135	135	104	.77
1	Apr. 21-23, 1967	466	464	465	343	.74
	Apr. 16-18, 1968	452	502	502	389	.77
2	Apr. 19, 20, 1967	436	386	429	384	.90
3	Apr. 24-26, 1967	408	411	410	401	.98
1	June 9-11, 1967	600	599	599	254	.42
2	June 7, 8, 1967	664	671	669	531	.79
3	June 12-14, 1967	527	523	525	443	.84
1	Aug. 26-28, 1967	275	260	266	78	.29
2	Aug. 22-24, 1967	277	328	308	162	.53
3	Aug. 29, 30, 1967	504	484	492	338	.69
1	Nov. 28, 29, 1967	204	-	204	86	.42

Note 1 - Radiation data in column 5 are estimated unobstructed horizon values for Connetquot River based on data from Mineola and Brookhaven (cols. 3,4).

Note 2 - Solar site 1 is typically heavily forested, solar site 2 is moderately to heavily forested, and solar site 3 is moderately forested.

Suppose the user is interested in predicting how the removal of the riparian vegetative cover might effect $\bar{E}$. Consider the period 22-24 August, 1967, when the Connetquot River received 162 langleys/day of a possible 308 langleys/day of whortwave solar radiation. Representative meteorological conditions at this time were:

$T_a = 65^0F$
$u = 2$ mph
cloud cover fraction = 0.5
relative humidity = 80%

The steps in solving for $\bar{E}$ are as follows:

1. Data have been gathered, as previously listed.

2. $H_{sn} = 162\ (3.7) = 600$ BTU/ ft^2/day. This value assumes that the vegetative canopy blocks 47% of the solar radiation. From Table IV-23, H_{an} is (.5 cloud cover at 65^0F) 2497 BTU/ ft^2/day. Thus,

   $$H_R = 2497 + 600 = 3097 \text{ BTU/ } ft^2\text{/day.}$$

3. At 80% relative humidity and an air temperature of 65^0F, $e_a = 12.5$ mmHg from Table IV-24.

4. As an initial guess of E, assume $E_1 = 65^0F$, the air temperature.

5. From Table IV-25, $B = .56$, $C(B) = -20.1$

6. $K = 15.7 + (.26 + .56)\ (11.4)\ (2) = 34.4$

7. $F(E_1) = \frac{-0.05(65)^2}{34.4} + \frac{3098-1801}{34.4} + \frac{34.4-15.7}{34.4(.26+.56)}$

$$\times \left[12.5 + 20.1 + .26(65)\right] = -6.1 + 37.7 + 33.0 = 64.6$$

8. $E_2 = .3(65) + .7(64.6) = 64.7$

9. Since $|E_2 - E_1| < 1^\circ F$ $\qquad \underline{\underline{\bar{E} = 64.7^\circ F}}$

Now suppose the user wants to find $\bar{E}$ for no reduction in H_{sn} due to shading. Steps 1 through 9 again are repeated, using $H_{sn} = 308(3.7) = 1140$ BTU/ft^2/day, with otherwise the same meteorological conditions. Without detailing the calculations here, it is found that $\bar{E} = 73.7^\circ$, a $9^\circ F$ increase.

It is evident then that altering the solar radiation penetrating to the stream can significantly change $\bar{E}$. Even more severe cases of repression of shortwave radiation (as noted by the 71% reduction on 26-28 August, 1967, Table IV-26) are possible, exemplifying the large differences which may be observed.

END OF EXAMPLE IV-10

The approach illustrated in Example IV-10 for predicting equilibrium temperature is obviously time consuming, and has been programmed for hand held calculators in Mills et al. (1979). A simplified approach is also available for predicting equilibrium temperature (Brady et al., 1969) and is described below. The predictions are usually within 3°F or less of those found by the more complicated approach.

The data required for the simpler approach are:

- T_d, dewpoint temperature ($^\circ F$)
- U, mean daily wind speed (mph), and
- H_{sn}, net incoming shortwave radiation (Btu/ft^2/day)

Short wave solar radiation data were previously shown in Figure IV-27. The climatic atlas (U.S. Department of Commerce, 1968) contains compilations of dewpoint temperature and windspeed. Figures IV-28 and IV-29 show these data for the months of July and August. Figures IV-27 through IV-29 provide the user with all the data needed to predict equilibrium temperature using Brady et al's approach.

To find the equilibrium temperature the following equations are applied sequentially:

COMPUTE ONCE ⟶

$$F(U) = 70 + 0.7\,U^2 \tag{IV-61}$$

ITERATE OVER THESE EQUATIONS

$$T = \left(E_i + T_D\right) / 2 \tag{IV-62}$$

$$B = 0.255 - 0.0085T + 0.000204T^2 \tag{IV-63}$$

$$K = 15.7 + \left(B + .26\right) F(u) \tag{IV-64}$$

$$E_{i+1} = T_D + H_S / K \tag{IV-65}$$

The wind speed function f(U) is found once from Equation IV-61. The dewpoint temperature (T_d) is a convenient starting choice as an initial guess of the equilibrium temperature. T can then be calculated from Equation IV-62; B from Equation IV-63; K from Equation IV-64; and finally a new equilibrium temperature (E_{i+1}) from Equation IV-65. If E_i and E_{i+1} differ by more than 1°F, return to Equation IV-62 with E_{i+1} and repeat the procedure until convergence is attained (usually within 2 or 3 cycles).

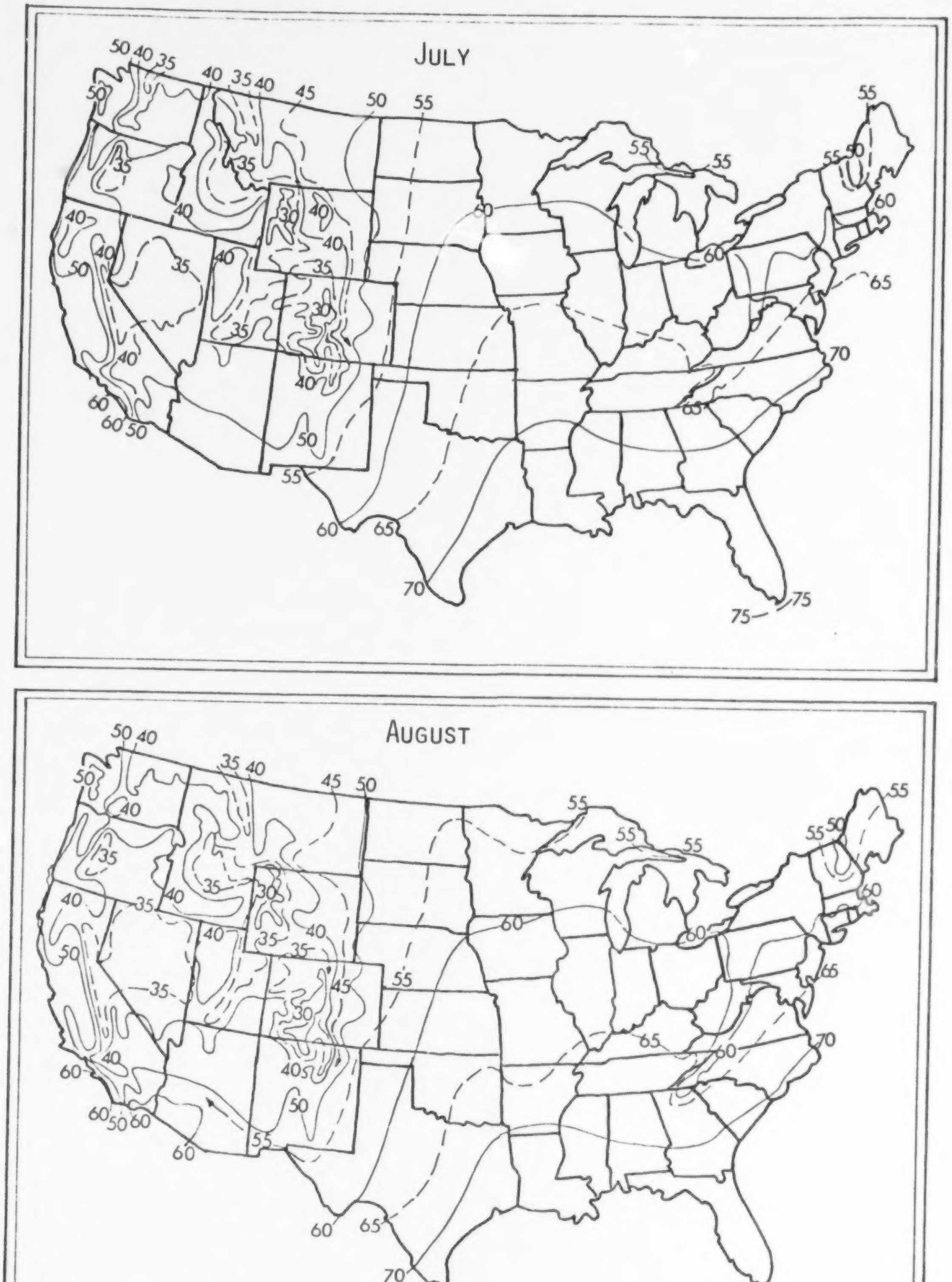
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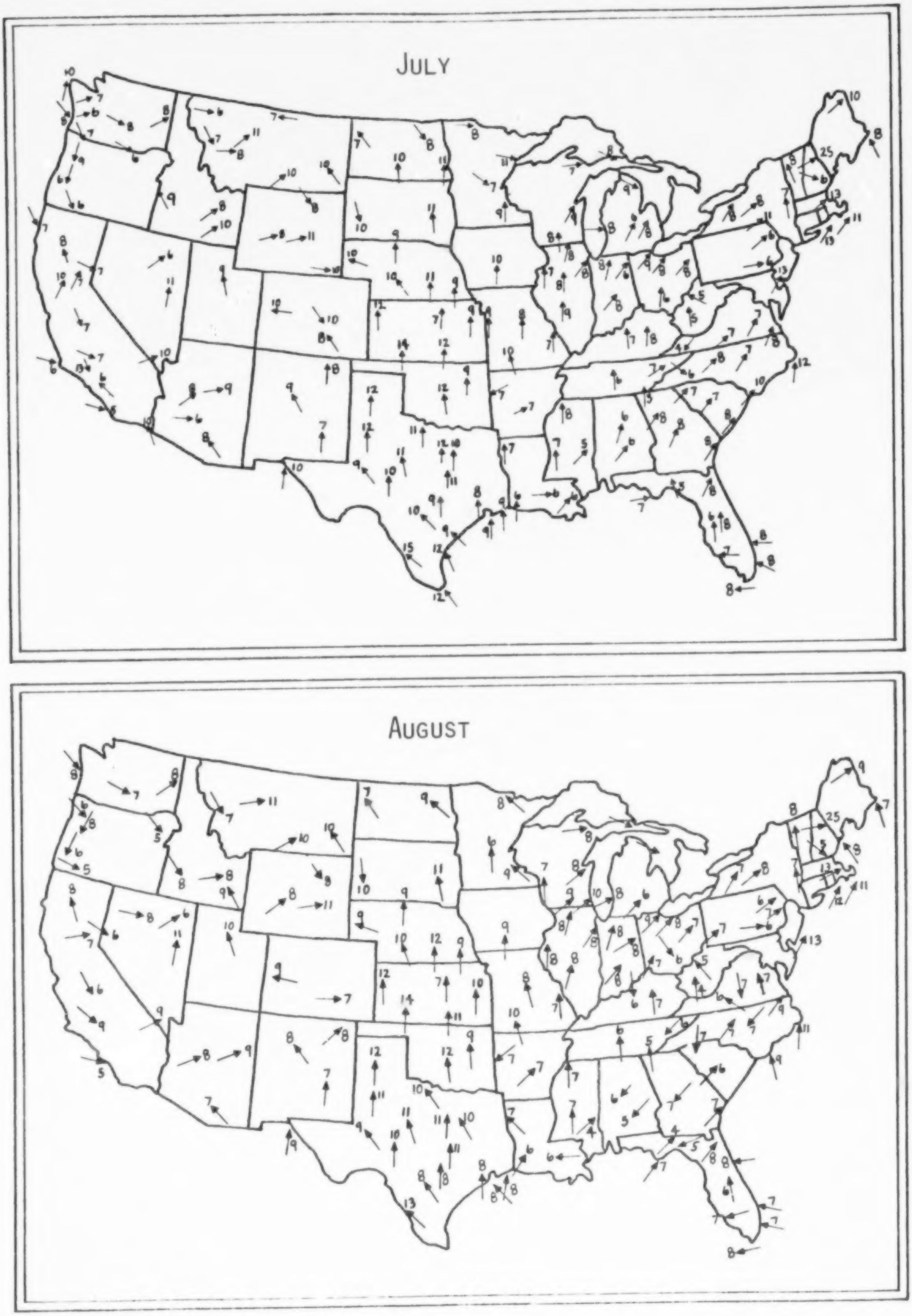
FIGURE IV-28 MEAN DEWPOINT TEMPERATURE (°F) THROUGHOUT THE UNITED STATES FOR JULY AND AUGUST (U.S. DEPARTMENT OF COMMERCE, 1968)



JULY

AUGUST

FIGURE IV-29 MEAN DAILY WIND SPEEDS (MPH) THROUGHOUT THE UNITED STATES FOR JULY AND AUGUST (U.S. DEPARTMENT OF COMMERCE, 1968)

EXAMPLE IV-11

Equilibrium Temperature using Simplified Approach

Determine the average daily surface water equilibrium temperature for Little Rock, Arkansas during the month of August. Based on Figures IV-27 through IV-29 the following data are found:

T_d = 68^oF
U = 7 mph
H_{sn} = $(525)(3.7) = 1943$ Btu/ft^2/day

Assume as a first guess That $E = T_d = 68^oF$

then

$f(U) = 70 + .7\ (7)^2 = 104.$
$T = (T_d + T_d)/2 = 68^o$
$B = .62$
$K = 15.7 + (.62 + .26)\ (104) = 107.$
$E = 68 + 1943/107 = 86^oF$

For the second interation

$T = (86 + 68)/2 = 77$
$B = 0.81$
$K = 127$
$E = 83.3^oF$

At the end of a third interation $E = 83.7^oF$, so convergence has been attained by three interations.

As a comparison, the equilibrium temperature will also be calculated using the longer approach. The required data are:

$T_a = 80^{\circ}F$
$T_d = 68^{\circ}F$
$U = 7.$
$H_{sn} = 1943$
sky cover = 0.5 (from climatic atlas)

A summary of the procedure is:

1. $H_{an} = 2958$
   $H_R = 1943 + 2958 = 4901$

2. Since $T_d = 68^{\circ}$, $e = 17.4$

3. Choose $E = T_a = 80^{\circ}F$

4. $B = .881$
   $C(B) = -37.6$

5. $f(U) = 70 + 0.7\ (7)^2 = 104$
   $K = 15.7 + (0.26 + .881)\ (104) = 134$

6. $F(E) = 79.3$

7. $E = .3(80) + .7\ (79.3) = 80^{\circ}F$, after one pass.

Since the starting guess of $80^{\circ}F$ is virtually identical with the calculated value at step 7, a second interation is not required. The two procedures predict equilibrium temperatures which differ by about $4^{\circ}F$.

END OF EXAMPLE IV-11

To estimate the effects of shading, the incoming solar radiation should be calculated first assuming no shading, but otherwise using existing meteorological conditions for the time of the year of interest. The effects of shading should be superimposed upon this result as a percent reduction. The following (Pluhowski, 1968) can serve as guidelines in estimating solar radiation reduction:

- 0-25 percent reduction: shading generally restricted to early morning and late afternoon

- 25-50 percent reduction: some sunshine penetration in morning and evening. Considerable sunshine between 1000 and 1400 hours.

- 50-75 percent reduction: very little sunshine penetration in morning or late afternoon. Some sunshine between 1000 and 1400 hours.

- Greater than 75 percent reduction: very little penetration even at noon.

4.4.4 Screening of Thermal Discharges

4.4.4.1 Introduction

This section presents a set of procedures which can be used to determine whether the thermal discharge at a proposed power plant site or the discharge from the expansion of an existing site is likely to violate thermal standards. Procedures are presented to test for contravention of the following types of standards:

- The ΔT Criterion: The increase in temperature of water passing through the condenser must not exceed a specified maximum.

- The Maximum Discharge Temperature Criterion: The temperature of the heated effluent must not exceed a specified maximum.

- The Thermal Block Criterion: The cross-sectional area of a river occupied by temperatures greater than a specified value must not exceed a specified percentage of the total area.

- The Surface Area Criterion: The surface area covered by isotherms exceeding a specified temperature increment (above ambient) must not exceed a specified maximum.

Actual values associated with the above standards vary by political jurisdiction. Accordingly, regulations must be consulted.

The thermal discharge screening procedures are designed to address the following questions:

- Is the power plant, as proposed, acceptable at the candidate location?

- What is the largest power plant that can be placed at the candidate location? Equivalently, can an existing power plant at the candidate location be expanded?

The methods do not analyze interactions among multiple powerplants on the same river. Such an analysis can be rather more complex. A report by Tetra Tech (1978) addresses that question.

The methods developed to evaluate instream thermal criteria use heat balance equations assuming a steady-state, well mixed system at low flow. The power plants are assumed to employ once through cooling, as shown in Figure IV-30.

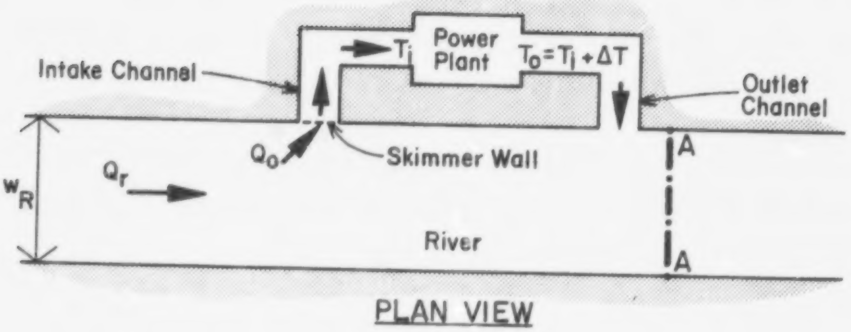


FIGURE IV-30 IDEALIZATION OF A RUN-OF-THE-RIVER POWER PLANT

The selection of well mixed conditions appears to be justified. Studies by Stefan and Gulliver (1978) on the Mississippi and Missouri Rivers have dealt with the lateral mixing of thermal plumes which were released at the shoreline and were not initially well mixed across the river. The investigators found that over a short distance, thermal losses were negligible and that the well mixed isotherm (the isotherm that would result were the plume initially well mixed laterally and vertically) eventually extended across nearly the entire width of the river, albeit at some distance downstream. This indicates that if the thermal block criterion is not met for the well mixed case, it is not likely to be met for the shoreline discharge either. A similar conclusion can be reached regarding the surface area constraint. Thus, at this level of analysis, it is not necessary to consider the consequence of incomplete lateral or vertical mixing adjacent to the shoreline discharge.

One simplification which can be used at the option of the user for the surface area calculation should be mentioned. Surface water that is undisturbed by anthropogenic influences (in a thermal sense) approaches the equilibrium temperature. This temperature is dictated by natural meteorological conditions. Surface water temperature in rivers, especially during steady low-flow periods, can be near equilibrium. In calculating the surface area occupied by isotherms exceeding a specified temperature it is necessary to know the equilibrium temperature. However, since the procedure for calculating equilibrium temperature is fairly complicated, considerable savings in computational effort can be obtained by assuming the ambient water is at its equilibrium temperature.

Some circumstances, in addition to anthropogenic influences, tend to produce ambient temperatures different from equilibrium. For example,

- Locally, large quantities of groundwater may discharge into the river.
- Hypolimnionic releases from large reservoirs may occur nearby.
- Snow melt may supply a substantial amount of inflow.

As a result of the first two influences, the stream water temperature may be lower than equilibrium since the source of the water comprising the stream flow has been shielded from the heating effect of solar radiation. Snow melt, although not likely to influence the river's thermal regime during the late summer, can be important through spring and into early summer in areas where high-mountain snowpack exists over most, or all, of the year.

The screening procedure that follows assumes the river water, once it has been heated by the thermal plume, is above equilibrium. This means that the water temperature will then decrease in the downstream direction, which is generally, but not always, true.

Table IV-27 shows the data needed to apply the thermal screening methods. The symbols are defined in the table and suggested default values are given for variables where appropriate. The variables are introduced in the table in the order they occur in the screening procedure.

TABLE IV-27

DATA NEEDED FOR THERMAL DISCHARGE SCREENING

Variable	Term Definition	Default Value
Mwe	Capacity of power plant in megawatts electric (bus bar)	--
e_p	Percent of total energy produced that goes to electricity production	new fossil fuel plants:38 nuclear plants:32
e_c	Percent of total energy produced that is dissipated through the cooling water	new fossil fuel plants:48 nuclear plants:68
Q_r	River flow rate above power plant (m^3/s)	$7Q_{10}$
ρ	Mass density of water (kg/m^3)	1000
C_p	Specific heat of water (Btu/°F-kg)	2.2
ΔT_{tb}	Temperature rise in the river cross section that constitutes a thermal block (°F)	5
ΔT_{max1}	Maximum legal allowable temperature rise across the condenser (°F)	20
ΔT_{max2}	Maximum allowable temperature rise across the condenser such that $T_e \leq (T_e)_{max}$ (°F)	--
T_e	Temperature of heated effluent (°F)	--
$(T_e)_{max}$	Maximum legal allowable temperature of heated effluent (°F)	86
ΔT_{maxmin}	The lesser of ΔT_{max1} and ΔT_{max2} (°F)	--
$(Q_p)_{max}$	The maximum allowable flow rate through the cooling system (m^3/s)	$.25Q_r$

TABLE IV-27 (continued)

Variable	Term Definition	Default Value
ΔT_{sa}	The isotherm defining the boundary of the surface area for which legal limits have been established (°F)	4
V	Mean velocity of the river (m/s)	
d	Mean hydraulic depth of river in reach under consideration (m)	--
E	Equilibrium temperature (°F)	--
K	Surface thermal transfer coefficient (Btu/d · °F · m^2)	--
A	Surface area of river down to ΔT_{sa} isotherm (m^2)	--
A_{sa}	Legal maximum surface area limit which can be covered by the ΔT_{sa} and greater isotherms (m^2)	--
W	Average surface width of river down to ΔT_{sa} isotherm (m)	--
T_{ra}	River temperature just above where a tributary joins the mainstem (°F)	--
T_t	Temperature of tributary (°F)	--
Q_t	Flow rate of tributary (m^3/s)	--
T_a	Air Temperature (°F)	--
Relative humidity	--	--
u	Wind speed at 7 meters above surface (m/s)	--
H_{sn}	Net shortwave solar radiation (Btu/m^2 · d)	
H_{an}	Net long wave solar radiation (Btu/m^2 · d)	--

4.4.4.2 Evaluating the Thermal Block Criterion

The initial temperature elevation that results when the thermal plume becomes well mixed with the river water is given as:

$$\Delta T_{wm} = \frac{Q_p}{Q_r} \Delta T \qquad \text{(IV-66)}$$

$$= \frac{1}{Q_r} \cdot \frac{e_c}{e_p} \text{MWe} \cdot \frac{1}{\rho C_p} \cdot \frac{3.414 \times 10^6}{3600} \qquad \text{(IV-67)}$$

where

ΔT_{wm} = temperature elevation of the initially well mixed isotherm (^oF)

Q_p = flowrate of cooling water (m^3/s)

ΔT = $T_e - T_r$ (^oF)

T_e = temperature of heated effluent (^oF)

T_r = temperature of river water upstream of power plant (^oF)

All other terms are defined in Table IV-27. To find ΔT_{wm}, Equation IV-67 is solved. If ΔT_{wm} is less than the thermal block temperature increment (ΔT_{tb}), the thermal block criterion is not contravened. Otherwise, it is.

4.4.4.3 Acceptability of the Temperature Rise Across the Condenser and of the Temperature of the Heated Effluent

Whether these criteria are met or not depends on a number of factors, such as the cooling water flow rate. Since the cooling water flow rate can be designed to be within a specified range, it is determined here whether a feasible range exists such that the two above mentioned criteria are met.

The minimum acceptable flow rate such that both temperature criteria do not exceed their standards is as follows:

$$(Q_p)_{min} = \frac{e_c}{e_D} \cdot \text{MWe} \cdot \frac{1}{\rho C_p \Delta T_{maxmin}} \cdot \frac{3.414 \times 10^6}{3600} \qquad \text{(IV-68)}$$

where

$(Q_p)_{min}$ = minimum flow rate such that the two temperature criteria are not exceeded (m^3/s)

By evaluating Equation IV-68 the minimum cooling water flow can be determined.

As an example of how ΔT_{maxmin} is chosen, suppose the following conditions exist:

- The maximum legal temperature rise across the condenser is 20^{0}F.
- The maximum legal temperature of the heated effluent is 86^{0}F.
- The ambient river temperature is 74^{0}F.

From these conditions, ΔT_{max2} (the allowable temperature increase across the condenser such that the temperature of the effluent does not exceed the legal maximum) = $86^{0}F - 74^{0}F = 12^{0}F$. So ΔT_{maxmin} = minimum ($20^{0}F$, $12^{0}F$) = 12^{0}F. 12^{0}F must be chosen, then, as the maximal temperature rise across the condenser.

Once Equation IV-68 has been solved, the ratio of cooling water to river flow should be checked so that the value is within acceptable limits. Equation IV-66 can be rewritten as:

$$\frac{Q_p}{Q_r} = \frac{\Delta T_{wm}}{\Delta T} \qquad \text{(IV-69)}$$

Since ΔT_{wm} has been calculated from Equation IV-67 and ΔT has been calculated as ΔT_{maxmin}, the flow rate fraction can be calculated from Equation IV-69. If this fraction exceeds a certain percent (e.g. 25 percent or some user defined value), then the cooling water flow rate is too large to be acceptable. If the flow rate fraction is not excessive, the actual flow rate can be chosen so that:

$$(Q_p)_{min} \leq Q_p \leq (Q_p)_{max} \qquad \text{(IV-70)}$$

where

$(Q_p)_{max}$ = maximum allowable cooling water flow rate (m^3/s)

4.4.4.4 Evaluating the Surface Area Constraint

The evaluation of this criterion may require the user to perform considerably more calculations than for any of the other prescreening criteria. The two major complicating factors that are encountered are: 1. determining the river equilibrium temperature, and 2. evaluating the effects of tributaries.

If it is the case that ΔT_{wm} does not exceed ΔT_{sa} the surface area criterion will not be contravened and no calculations have to be performed. If ΔT_{wm} exceeds ΔT_{sa}, the criterion might be exceeded. In this case it is necessary to determine the distance from the location of the thermal discharge to the downstream location of the ΔT_{sa} isotherm. This distance is given by:

$$x_{sa} = \frac{-\rho C_p V d}{K} \ln \left(\frac{T_{sa} - E}{T_{wm} - E} \right) 24 \cdot 3600 \qquad \text{(IV-71)}$$

where

$T_{sa} = \Delta T_{sa} + T_r$

$T_{wm} = \Delta T_{wm} + T_r$

Section 4.4.3 discusses procedures for predicting K and E. Once K and E are found, x_{sa} can be determined from Equation IV-71. If one or more tributaries exist with the distance x_{sa}, then x_{sa} should be recalculated as discussed in Section 4.4.4.5.

The surface area included within this reach is:

$$A = x_{sa} \cdot W \qquad \text{(IV-72)}$$

where

A = surface area of the river from the point of thermal discharge to x_{sa} (m^2)

W = average river width in this reach (m)

If $A < A_{sa}$ then the surface area criterion is not contravened. Otherwise, it is.

4.4.4.5 Evaluating the Effects of a Tributary in Mitigating Temperature Within a Thermal Plume

Tributaries, when they join a river subjected to the influences of a thermal plume, generally act to reduce the elevated river temperature. They may therefore prevent the surface area constraint from being exceeded when it otherwise would.

Equation IV-71 assumes no tributaries exist throughout the reach defined by x_{sa}. If it is found that $x_{sa} > x_t$ (x_t is defined below under Equation IV-73) then it is necessary to examine the impact of the tributary flow on the surface area constraint. This is done by computing the water temperature (^{O}F) just above the location where the tributary joins the mainstream using the following equation:

$$T_{ra} = \left(T_{wm} - E\right) \exp\left(\frac{-Kx_t}{\rho C_p Vd \cdot 24 \cdot 3600}\right) + E \qquad \text{(IV-73)}$$

where

T_{ra} = river temperature just upstream of tributary (^{O}F)

x_t = distance from power plant discharge to tributary (m)

After the river has mixed with the tributary the new river temperature (^{O}F) is given by:

$$\left(T_r\right)_{new} = \frac{T_{ra}Q_r + T_tQ_t}{Q_r + Q_t} \qquad \text{(IV-74)}$$

where

T_t = temperature of the tributary (^oF)
Q_t = flow rate of tributary (m^3/s)

If

$$\left(T_r\right)_{new} \leq \Delta T_{sa} + T_{ra} \qquad \text{(IV-75)}$$

then this location marks the downstream location of the ΔT_{sa} isotherm and the surface area A can be calculated using the distance x_{sa} as the distance down to the tributary, x_t. Otherwise the ΔT_{sa} isotherm is located further downstream. In this case Equation IV-71 is reapplied (first making appropriate adjustments to V and d) where the initial temperature is $(T_r)_{new}$ (which was T_{wm} in Equation IV-71) and the final temperature is still T_{sa}. The distance x_{sa} is determined by adding this additional distance to x_t.

4.4.4.6 Determining Whether the Thermal Block or the Surface Area Constraint is the More Limiting

One of these two constraints may cause a greater limitation on power plant size than the other. If $\Delta T_{tb} < \Delta T_{sa}$ the thermal block constraint will be more limiting, and there is no need to continue with the analysis in this part. If, however, $\Delta T_{tb} > \Delta T_{sa}$, the surface area constraint may be more limiting. To determine if it is, find ΔT_{wm} (call it ΔT_{wmsa}) using the following equation:

$$\Delta T_{wmsa} = E + \left(T_{sa} - E\right) \exp\left(\frac{-Kx_{sa}}{\rho C_p Vd \cdot 24 \cdot 3600}\right) - T_r \qquad \text{(IV-76)}$$

where

$$T_{sa} = \Delta T_{sa} + T_r \qquad \text{(IV-77)}$$

and

$$x_{sa} = \frac{A_{sa}}{W} \qquad \text{(IV-78)}$$

If a tributary exists in the reach delineated by x_{sa}, recompute x_{sa} as outlined in Section 4.4.4.5.

If $\Delta T_{wmsa} < \Delta T_{tb}$, the surface area constraint is more restrictive, so set $\Delta T_{wm} = \Delta T_{wmsa}$. Otherwise set $\Delta T_{wm} = \Delta T_{tb}$.

4.4.4.7 Determining the Maximum Plant Capacity

The maximum power plant capacity can be determined based upon the maximum well mixed temperature elevation and the river flow rate. It is given by:

$$(\mathrm{MWe})_{max} = \frac{e_p}{e_c} \cdot \rho C_p \cdot (Q_p \Delta T)_{max} \frac{3600}{3.414 \times 10^6} \qquad \text{(IV-79)}$$

$$= \frac{e_p}{e_c} \cdot \rho C_p \cdot \Delta T_{wm} Q_r \cdot \frac{3600}{3.4.4 \times 10^6} \qquad \text{(IV-80)}$$

By using Equation IV-80 and the maximum allowable ΔT_{wm}, the maximum capacity can be found.

4.4.4.8 Readjusting the Maximum Cooling Water Flow Rate

If the minimum acceptable flow rate is greater than the maximum allowable, the power plant size must be reduced. To do this, set

$$Q_p = (Q_p)_{max} \qquad \text{(IV-81)}$$

where

Q_p = actual cooling water flow rate (m^3/s)
$(Q_p)_{max}$ = maximum allowable cooling water flow rate (m^3/s)

ΔT_{wm} is recalculated by:

(Note: the surface area and thermal block constraints are still met and need not be recomputed.)

$$\Delta T_{wm} = \Delta T_{maxmin} \frac{(Q_p)_{max}}{Q_r} \qquad \text{(IV-82)}$$

where

ΔT_{maxmin} is the same ΔT calculated earlier.

EXAMPLE IV-12

Estimating ΔT Across a Power Plant Heat Exchange Unit

Suppose the user wants to determine ΔT for the Hartford Electric Light Company's South Meadow Steam Electric Power Plant (a fossil fuel plant) located on the Connecticut River. Data available are (Jones *et al.*, 1975):

capacity	217 MW
cooling water flow rate	341 ft^3/sec
waste heat discharged to cooling water	422 MW

Since the waste heat being dissipated through the cooling water is known, ΔT can be calculated directly using that value in conjunction with the known flow rate. Assume, however, that the waste heat being discharged is not known. It can be estimated from the plant capacity as follows. First, assume the plant efficiency is 33 percent. The rate at which fuel is burned when at capacity is then:

$$\frac{217}{.33} = 658 \text{ MW}$$

If 10 percent of the total energy is lost up the stacks, then approximately 58 percent is dissipated through the cooling water, or

$$658\ (.58) = 382 \text{ MW}$$

Compared with the known 422 MW of heat discharged to the cooling water, the above calculation would underestimate ΔT.

ΔT is calculated by

$$\Delta T = \frac{\text{thermal loading rate to cooling water in megawatts}}{\gamma C_p Q_o} \ X$$

$$(3.414)\left(10^6 \ \frac{BTU}{hr/_{MW}}\right)\left(\frac{1 \ hr}{3600 \ sec.}\right) \qquad \text{(IV-83)}$$

where

γC = 62.4 $BTU/ft^3/{}^oF$

Q_o = flow rate, ft^3/sec

Substituting the appropriate values into the above equation, it is found that (using the known thermal loading to the cooling water):

$$\Delta T = \frac{(422) \ (3.414) \ (10^6)/3600}{(62.4) \ (341)} = 18.8^oF$$

Equation IV-83 is not feasible to use when the thermal loading rate to the cooling water is unknown. As an alternative approach, the following expression can be employed:

$$\Delta T = \frac{1}{Q_o} \cdot \frac{e_c}{e_p} \ MWe \cdot \frac{1}{\rho C_p} \cdot \frac{3.414 \times 10^6}{3600} \qquad \text{(IV-84)}$$

where

e_p = percent of total energy produced that is transmitted as electricity. For new fossil fuel plants: 38 percent: for nuclear plants: 32 percent.

e_c = percent of total energy produced that is dissipated through cooling water. For new fossil fuel plants: 48 percent; for nuclear plants: 68 percent

MWe = capacity of power plant in megawatts electric

Equation IV-84 predicts that ΔT is

$$\frac{1}{341} \cdot \frac{58}{32} \cdot 217 \ \frac{1}{62.4} \cdot \frac{3.414 \quad 10^6}{3600} = 17.5°F$$

ΔT is only about $1^{\circ}F$ less than predicted by Equation IV-83.

END OF EXAMPLE IV-12

4.4.5 Longitudinal Temperature Variation

If the temperature at a particular location in a river is known, the steady-state temperature distribution downstream from that point can be estimated by:

$$\frac{T - E}{T_m - E} = \exp\left(\frac{-.061 \cdot Kx}{\rho C_p U d}\right) \qquad \text{(IV-85)}$$

where

T_m = temperature at x = 0, °F

T = stream temperature at a distance x, where x is measured in miles

E = equilibrium temperature, °F

K = thermal transfer coefficient, BTU/ft²/day/°F

U = stream velocity, ft/sec

d = stream depth, feet

ρ = water density, lb/ft³

C_p = heat capacity of water, BTU/lb/°F (ρC_p = 62.4 BTU/ft³/°F)

An important fact is revealed upon inspection of Equation IV-85. Suppose that a thermal discharge heats the ambient water to a temperature T_m, but T_m is less than the instantaneous equilibrium temperature E. In that instance the stream temperature will continue to rise exponentially downstream, approaching E. The rate at which T approaches E is dependent on the thermal transfer coefficient, as well as stream velocity and depth. Equation IV-66 is graphically illustrated in Figure IV-31.

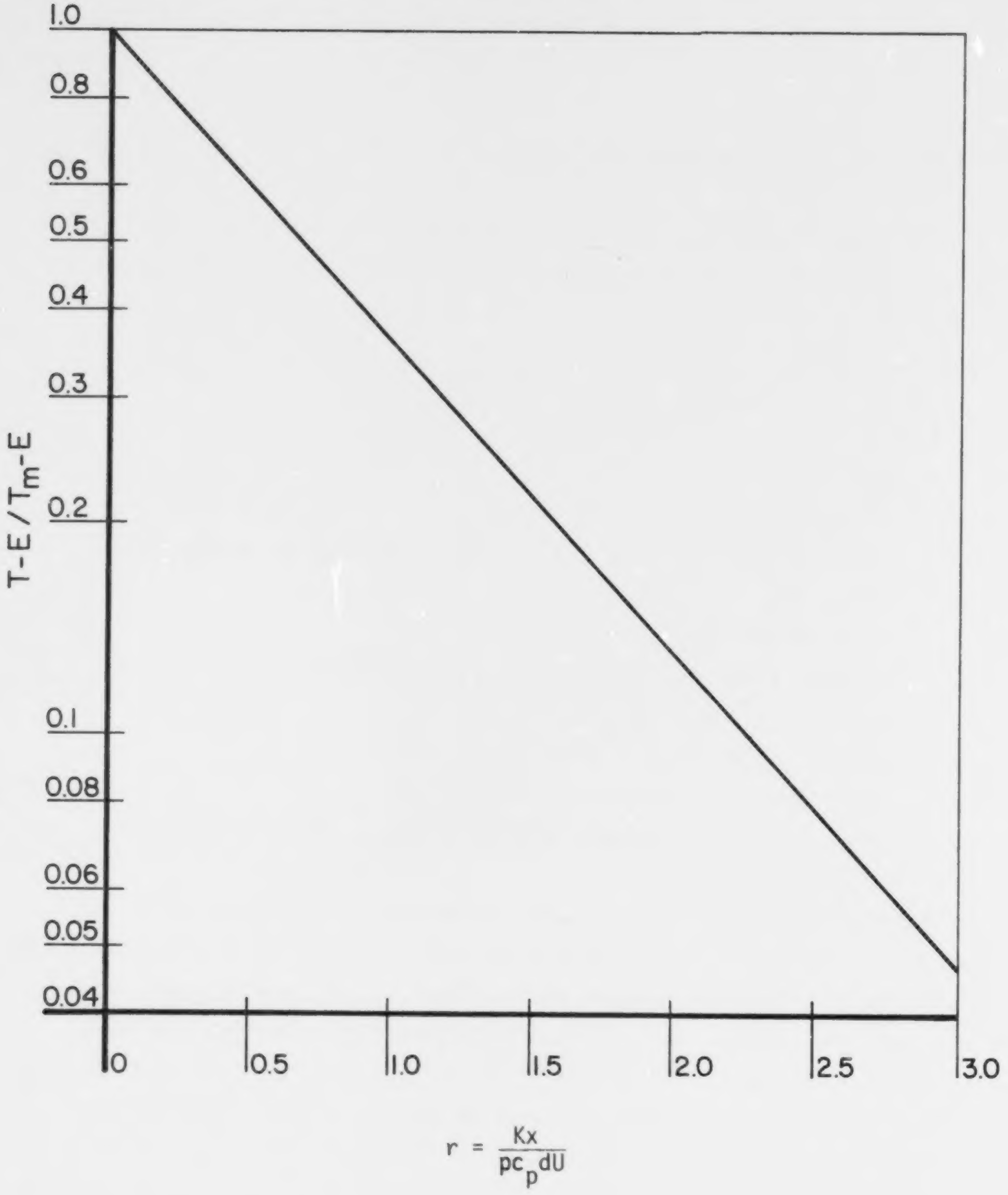


FIGURE IV-31 DOWNSTREAM TEMPERATURE PROFILE FOR COMPLETELY MIXED STREAM, T-E/T_M-E VS. r (FROM EDINGER, 1965)

EXAMPLE IV-13

Use of Figure IV-31

Suppose an average daily thermal transfer coefficient, K, of 200 BTU/ft^2/day has been calculated. The river of interest has an initial temperature "excess" (i.e. $T_m - E > 0$). How far downstream will that excess be 50 percent of the original? Other stream data:

$U = .5$ fps
$d = 4$ feet
$\rho C_p = 62.4$ BTU/ft^3/^{o}F

From Figure IV-31, r is to be found such that

$$\frac{T - E}{T_m - E} = .5$$

The correct r equals 0.68. Solving for x in terms of r it is found:

$$x = \frac{r \rho C_p dU}{K} = \frac{(0.68)\ (62.4)\ (4)\ (.5)(24)(3600)}{200}$$

$$= 3.6 \times 10^4 \text{ feet} = 6.9 \text{ miles}$$

The associated travel time is $T = \frac{3.6 \times 10^4}{.5} \times \frac{1}{3600}$ hr = 20.4 hours

END OF EXAMPLE IV-13

4.4.6 Diurnal Temperature Variation

Although it is beyond the scope of this report to analyze diurnal stream temperature variations, a few brief statements should be made. Diurnal stream temperature variations on Long Island, New York, were mentioned in Section 4.4.1. Documentation of large diurnal temperature variations is not limited to New York. For example, studies in Oregon (Brown, 1969), Hawaii (Hathaway, 1978) and California (Mills, 1979) have revealed that solar radiation entering shallow streams and rivers produces a significant difference between maximum and minimum daily temperatures. Figure IV-32 shows one such example on the Santa Ana River near Mentone, California (Mills, 1979). The water temperature varied by 17°F over a period of 24 hours. One significant effect of the temperature variation is its effect on dissolved oxygen levels. Figure IV-33 shows the measured dissolved oxygen concentrations and predicted saturation levels over the same time period at the same location on the Santa Ana River. The dissolved oxygen concentrations ranged from a high of 9.2 mg/l to a low of 8.0 mg/l. The variations were caused predominantly by the temperature changes. This illustrates several points.

- Temperature data concomitant with dissolved oxygen data might be needed to properly interpret the cause of dissolved oxygen variations in shallow rivers receiving large amounts of solar radiation.
- Removing riparian vegetation around shallow rivers tends to increase the daily maximum temperature and decrease the daily minimum temperature.
- Impacts on the dissolved oxygen levels and indigenous biota can be significant.

4.4.7 Low Flow and Temperature

Evidence has previously been cited in this chapter to show that in many parts of the country high temperature conditions are concomitant with low flow. The planner needs to be able to quantify better the nebulous term "low flow" to fruitfully use this concept as a planning tool. For example, suppose a decision is made based on the low flow condition of this year. What are the chances that this low flow will be exceeded in the future? If they are high, then any decision (e.g. at particular level of waste abatement at a sewage treatment plant) based on the observed conditions could have unexpected deleterious results at a future time. It is paramount then, to predict how often flow will fall below a specified rate.

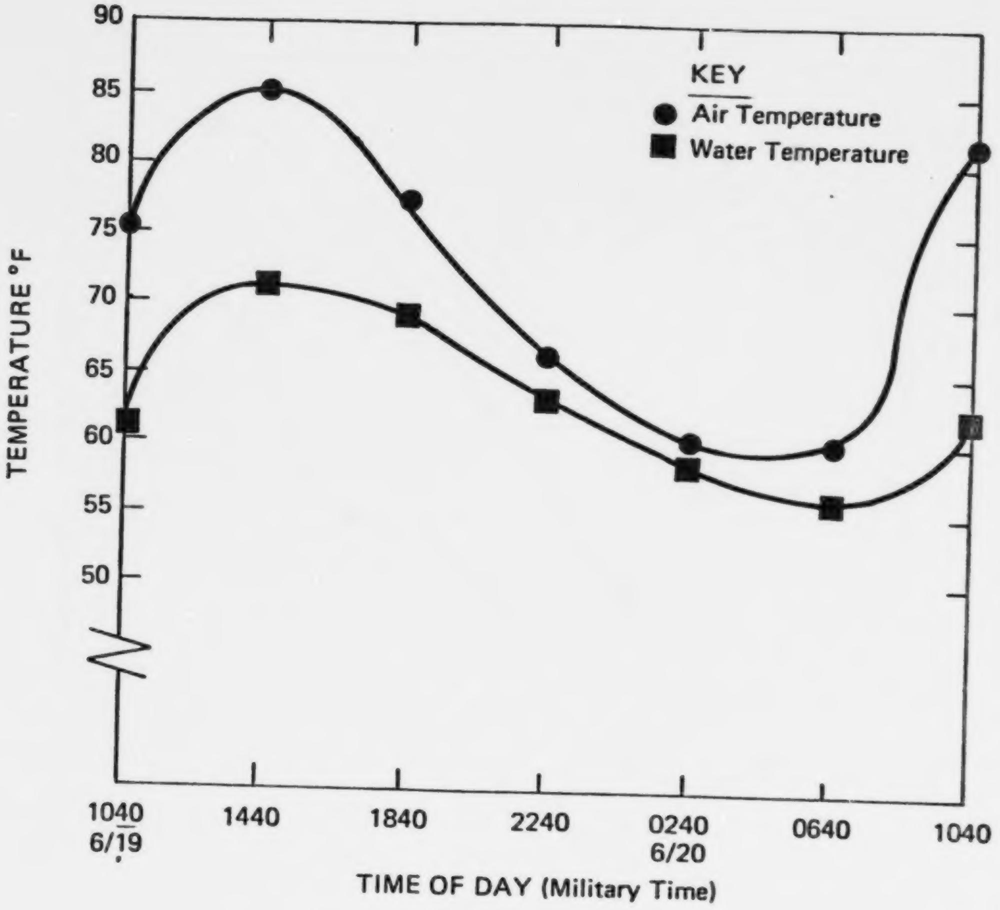


FIGURE IV-32 MEASURED AIR AND WATER TEMPERATURES FOR THE SANTA ANA RIVER NEAR MENTONE, CALIFORNIA, IN JUNE 1979.

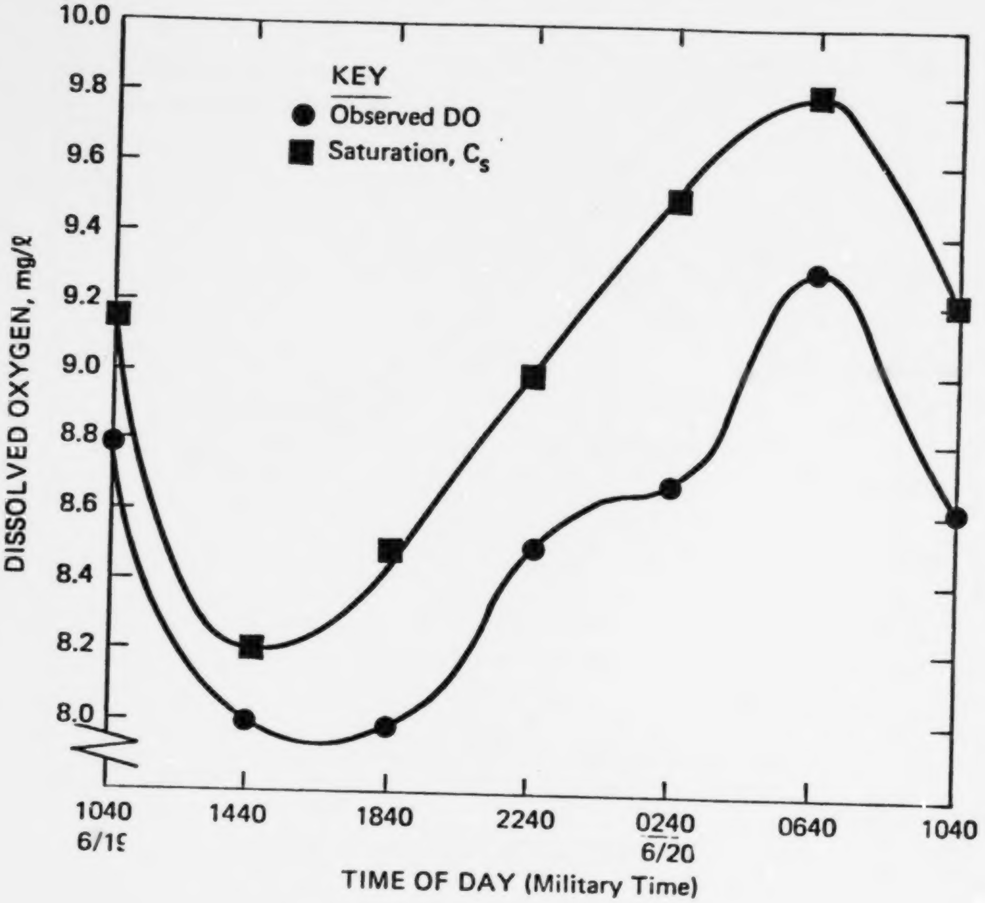


FIGURE IV-33 MEASURED DISSOLVED OXYGEN CONCENTRATION AND PREDICTED SATURATION CONCENTRATION FOR THE SANTA ANA RIVER NEAR MENTONE, CALIFORNIA, IN JUNE 1979.

Two measures or indices of low flow that have been found useful are flow duration and low-flow frequency. Although it is beyond the scope of this report to explain in detail how to develop these measures, examples of each will be presented that explain their utility. The majority of the material in this section is from Cragwall (1966) who provides a discussion on low flow, and cites additional references. Many texts on engineering hydrology (e.g. Linsley et al., 1958) also discuss low flow. Figure IV-34 shows a flow duration curve for the Hatchie River at Bolivar, Tennessee. The vertical axis is the daily discharge and the horizontal is the percent of time a flow is equaled or exceeded. For example, 95 percent of the time from 1930-58 the flow exceeded 177 cfs. It can also be assumed that this flow (177 cfs) will probably be exceeded 95 percent of the time in other years. Thus this concept offers one means by which to quantify "low flow".

A second concept is the low flow frequency curve, illustrated in Figure IV-35. This depicts the relationship between discharge and recurrence interval of different duration flows. For example the 7 day mean flow of 100 cfs can be expected to occur once each 19 years. Stated another way, since probability is the reciprocal of recurrence interval, in any one year there is about a 5 percent probability that a seven day mean flow of less than 100 cfs will occur. A commonly used flow for analyses is the 7 day mean flow at a recurrence interval of 10 years, or $7Q_{10}$.

4.4.8 Interrelationships Between Temperature Prediction Tools

The three major temperature prediction tools presented in Section 4.4 are:

- water temperature alterations caused by a power plant
- equilibrium temperature
- longitudinal river temperature profile

Figure IV-36 shows three river temperature profiles which illustrate how these tools can be used jointly. Curve A represents a temperature profile of a river where a power plant is located a distance D below some reference point. The temperature on the river above the power plant is T_2 which is

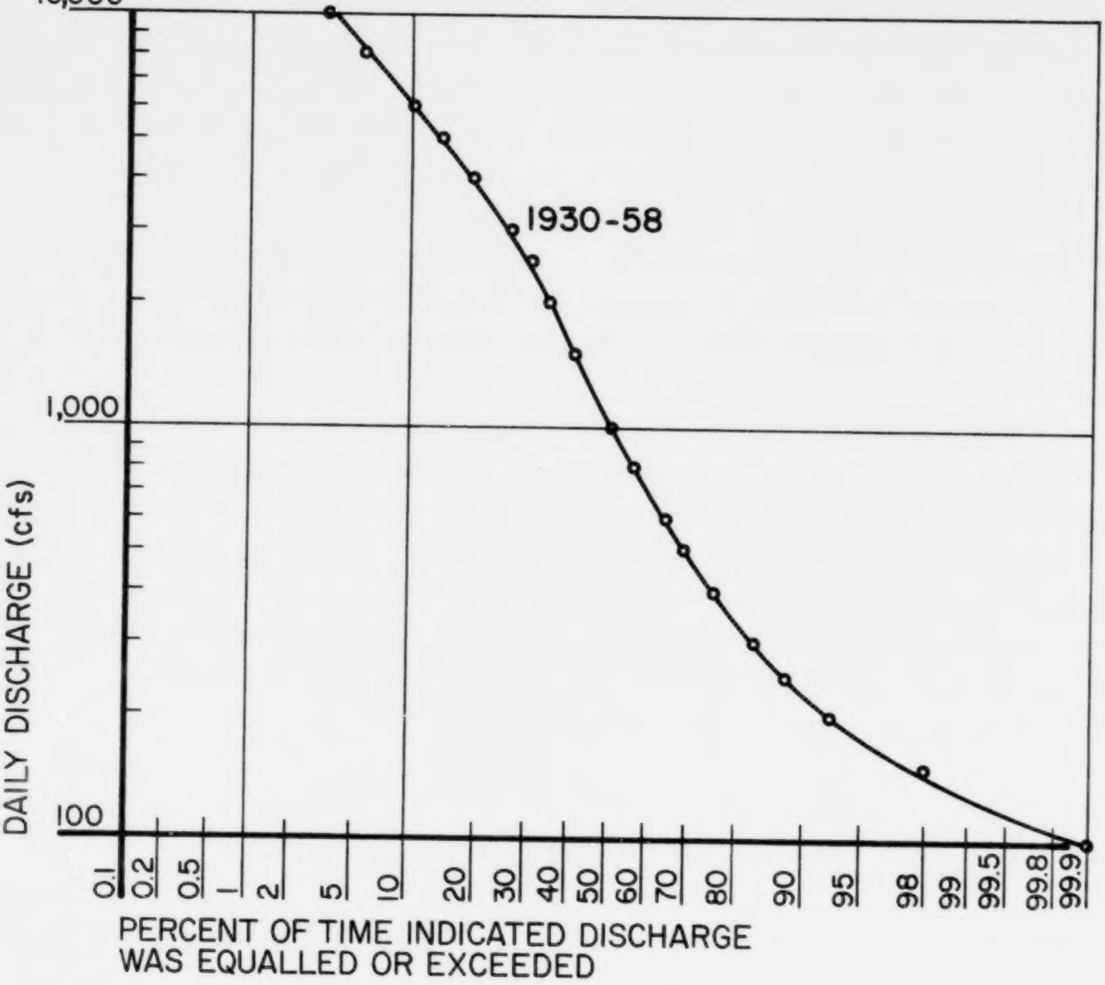


FIGURE IV-34 FLOW DURATION CURVE, HATCHIE RIVER AT BOLIVAR, TENN. (FROM CRAGWALL, 1966)

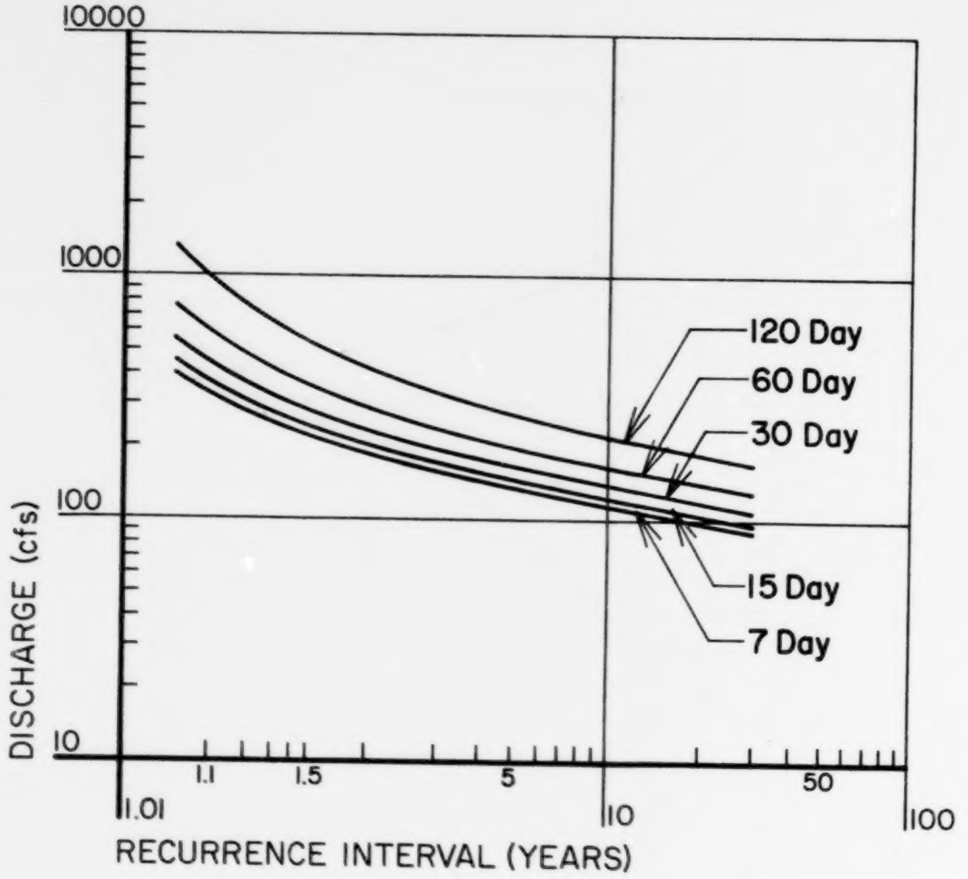


FIGURE IV-35 FREQUENCY OF LOWEST MEAN DISCHARGES OF INDICATED DURATION, HATCHIE RIVER AT BOLIVAR, TENN. (FROM CRAGWALL, 1966)

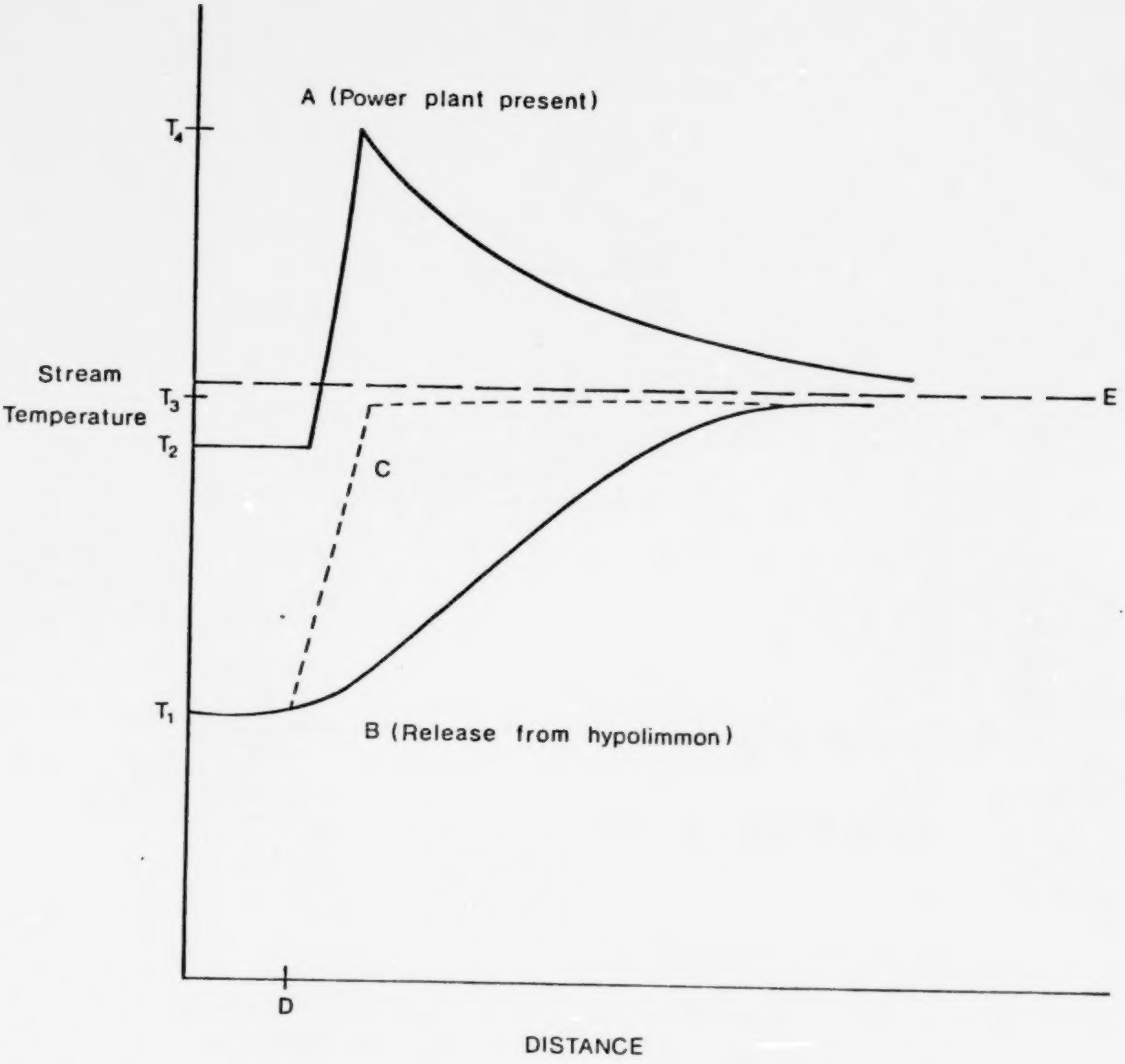


FIGURE IV-36 THREE RIVER TEMPERATURE PROFILES

slightly below the equilibrium temperature. Due to the thermal discharge from the power plant, the river's temperature is increased to T_4, above the equilibrium temperature. Below the mixing zone area, the water temperature gradually decreases toward equilibrium, as the excess heat is dissipated into the atmosphere.

Curve B illustrates the temperature profile of a river whose water comes predominantly from the hypolimnion of a reservoir. While in the reservoir the water is insolated from the solar radiation, so the temperature is below the equilibrium temperature. As the water is withdrawn from the reservoir and begins to flow downstream, its temperature increases due to solar radiation and atmospheric heating. The temperature tends to approach the same equilibrium temperature (the two rivers are assumed to be in the same geographic area).

Curve C shows the temperature profile of river B which now has a power plant, similar to the one on river A, discharging into it. If the flow rates of the two rivers are the same, so is the initial temperature increase (i.e. $T_3 - T_1 = T_4 - T_2$). However, the temperature of the river continues to increase, in contrast to profile A, because T_3 is less than E. This illustrates an unusual, but entirely possible, situation where river temperature continues to increase below a thermal discharge.

4.5 NUTRIENTS AND EUTROPHICATION POTENTIAL

4.5.1 Introduction

Within the past decade the elements most often responsible for accelerating eutrophication - nitrogen and phosphorus - have shown generally increasing levels in rivers (EPA, 1974). Median concentrations increased in the period from 1968 to 1972 over the period from 1963 to 1967 in 82 percent of the reaches sampled for total phosphorus, 74 percent for nitrate, and 56 percent for total phosphate.

These increasing concentrations afford more favorable conditions for eutrophication, although many rivers with high nutrient levels do not have algal blooms. Algal growth can be inhibited in numerous ways. For example, turbidity can decrease light transmittance through water and effectively stop growth. Decreasing turbidity could, however, have a deleterious side effect of promoting excessive algal growth, unless stream nutrient levels are concurrently decreased. High water velocity can also prevent algae from reaching bloom proportions before they are carried out of the river system. The eutrophication problem, then, is transferred to the water body into which the river empties.

4.5.2 Basic Theory

Stumm and Morgan (1970) have proposed a representation for the stoichiometry of algal growth:

$$\begin{array}{c} 106CO_2 + 16NO_3^- + HPO_4^{2-} + 122H_2O + 18H^+(+\text{ trace elements; energy}) \\ P \Big\downarrow \Big\uparrow R \\ \underset{\text{algal protoplasm}}{\{C_{106}H_{263}O_{110}N_{16}P_1\}} + 138\,O_2 \end{array} \qquad \text{(IV-86)}$$

where P and R represent photosynthesis and respiration, respectively. Observe that in the algal protoplasm the ratio of C:N:P is

$$C:N:P = 106:16:1, \text{ by atomic ratios} \qquad \text{(IV-87)}$$

$$C:N:P = 41:7:1, \text{ by weight ratios} \qquad \text{(IV-88)}$$

From the above two equations it can be inferred that only small amounts of phosphorus are needed to support algal growth in relation to the amounts of carbon and nitrogen required. If phosphorus is not present in the amount required for algal growth then algal production will be curtailed, regardless of how much of the other nutrients is available. Phosphorus is then termed growth limiting. It is possible for other elements, particularly nitrogen, and occasionally carbon or trace metals, to be growth limiting as well (Stumm and Stumm-Zollinger, 1972).

Nitrogen uptake by algae is generally in the nitrate form if nitrate is available. However, different types of fresh water algae can utilize either organic nitrogen or inorganic nitrogen in the form of ammonia, depending on what is available (Stumm and Stumm-Zollinger, 1972). Algae typically require phosphorus in an inorganic form, usually as orthophosphate ion (Kormondy, 1969).

Some indication of whether nitrogen or phosphorus is growth limiting may be made by determining the weight ratio of the appropriate forms of nitrogen and phosphorus found in a river, and comparing that with the stoichiometric ratio required for growth. This gives an idea regarding the nutrient on which control efforts should focus. Specifically, let

$$R = \frac{[TN]}{[OPO_4\text{-}P]} \qquad \text{(IV-89)}$$

where

$[TN]$ = concentration of total nitrogen in river, mg-N/l

$[OPO_4\text{-}P]$ = concentration of orthophosphate, mg-P/l

If $R > 10$, phosphorus is more likely to limit than N.

If $R < 5$, nitrogen is more likely limiting than P.

If $5 < R < 10$, a determination can not be made.

Since the N:P ratio in algal biomass can vary from species to species, this makes the determination of the limiting nutrient somewhat uncertain, and leads to the indeterminate range of $5<R<10$. If local data include an inventory of algal species present, then the N:P ratio of the known species should be used in lieu of Equation IV-88. Both Lehman, et al. (1975) and Lund (1965) provide specific algal data as well as further discussions.

The following table (Table IV-28) shows an approximate relationship between total nitrogen and total phosphorus concentrations and the potential algal biomass that can result. Both nitrogen and phosphorus must be present in the amounts shown for the resultant growth to occur.

TABLE IV-28

EUTROPHICATION POTENTIAL AS A FUNCTION OF NUTRIENT CONCENTRATIONS

P (mg-P/l)	N (mg-N/l)	Dry Algal Cells (mg/l)	Significance
0.013	0.092	1.45	Problem threshold
0.13	0.92	14.5	Problem likely to exist
1.3	9.2	145.0	Severe problems possible

4.5.3 Estimating Instream Nutrient Concentrations

Because of the transformations that occur among the different nitrogen and phosphorus compounds it is not possible to conveniently track any particular form of nitrogen or phosphorus through a stretch of river. However, if total nitrogen and total phosphorus can be considered conservative, a mass balance approach can be easily formulated for these constituents. In reality this assumption may not be met for a variety of reasons.

For example, algae utilize nutrients, die, and settle to the bottom. Although there is a recycling of algal cell-bound nutrients, the settling rate may surpass the rate of recycling. Assuming total nitrogen and total phosphorus to be conservative should give an estimate of the upper limit of the instream concentrations of these nutrients.

The instream concentration of total nitrogen (TN) or total phosphorus (TP) resulting from a point discharge is (formulas will be presented for TN only; those for TP are exactly analogous):

$$TN_o = \frac{TN_u Q_u + TN_w Q_w}{Q_u + Q_w} \tag{IV-90a}$$

or

$$TN_o = \frac{TN_u Q_u + w_p/5.38}{Q_u + Q_w} \tag{IV-90b}$$

where

TN_u = instream TN upstream of discharge. mg-N/l

TN_w = concentration of TN in point discharge, mg-N/l

Q_u = flow in river upstream of point discharge, cfs

Q_w = flow rate of point discharge, cfs

TN_o = resulting instream TN concentration, mg-N/l

w_p = loading rate of point source, lb/day

The expression for TN_o is given by either Equation IV-91A or IV-91B The appropriate form to use will depend on the form of the available data.

To determine the instream concentration of total nitrogen due to a distributed discharge, use:

$$TN = TN_o + \frac{\Delta_Q x}{Q} (TN_r - TN_o) \qquad \text{(IV-91a)}$$

or

$$TN = \frac{TN_o Q_o}{Q} + \frac{wx}{5.38\ Q} \qquad \text{(IV-91b)}$$

where

TN_r = TN entering with the distributed flow, mg-N/l
TN_o = instream TN at x = 0, mg-N/l
x = distance downstream from the point source discharge
Q = stream flow rate at x, cfs
Q_o = stream flow rate at x = 0, cfs
Δ_Q = incremental flow increase per unit distance, cfs/mile
w = mass flux of TN entering the stream through the distributed source, lb/day/mile

The choice of whether to use Equation IV-91a of IV-91b depends on the available data. Based on the approach detailed in Chapter III, the mass flux of nutrient entering the stream (in units of lb/day/mile) can be generated. When this approach is used, then Equation IV-91b is applicable.

To use Equation IV-91a the concentration of pollutant from the nonpoint source has to be known. This can be accomplished using the approach of Omernik (1977). Nonpoint source nitrogen and phosphorus concentrations are predicted as fractions of land use type or based on color coded maps if land use categories are not known. The data used to predict nitrogen and phosphorus concentrations were generated in a National Eutrophication Survey (NES) program wherein a nationwide network of 928 nonpoint-source watersheds were monitored. This method accounts for only the nonpoint source contribution. Consequently, if point source exist within the watershed, their contributions must be included as well in order to accurately predict instream concentrations.

Table IV-29 summarizes the predictive formulas developed by Omernik for total phosphorus, orthophosphorus, total nitrogen, and inorganic nitrogen. The formulas are regionalized by eastern, central, and western United States. Agricultural, urban, and forested lands comprise the independent variables in the formulas.

Omernik's analysis of the NES data indicates that:

1. Streams draining agricultural watersheds had considerably higher nutrient concentrations than those draining forested watersheds.

2. Nutrient concentrations were generally directly proportional to the percent of the land in agriculture and inversely proportional to the percent of land in forest.

3. Mean concentrations of total phosphorus and total nitrogen were nearly nine times greater in streams draining agricultural lands than in streams draining forested lands.

4. Mean phosphorus concentrations in streams draining forested watersheds in the west were generally twice as high as those in the east.

5. Total and inorganic nitrogen in streams draining agricultural watersheds were considerably higher in the heart of the corn belt than elsewhere.

As an alternative to the equations shown in Table IV-29, Omernik provides three colored maps of nonpoint source related concentrations of nutrients in streams. They can be used where detailed information necessary for more accurate prediction is unavailable.

TABLE IV-29

REGIONAL STREAM NUTRIENT CONCENTRATION PREDICTIVE MODELS

Nutrient Form Region	Model, Correlation Coefficient and Multiplicative Standard Error
Total phosphorus	
East	Log_{10} (PCONC) = -1.8364 + 0.00971 (% agric + % urb) r = 0.74, f = 1.85
Central	Log_{10} (PCONC) =-1.5697 + 0.00811 (% agric + % urb) -0.002312 (% for) r = 0.70, f = 2.05
West	Log_{10} (PCONC) =-1.1504 + 0.00460 (%agric + %urb) -0.00632 (% for) r = 0.70, f = 1.91
Orthophosphorus	
East	Log_{10} (OPCONC) = -2.2219 + 0.00934 (% agric + % urb) r = 0.73, f = 1.86
Central	Log_{10} (OPCONC) = -2.0815 + 0.00868 (% agric + % urb) r = 0.63, f = 2.05
West	Log_{10} (OPCONC) = -1.5513 + 0.00510 (% agric + % urb) -0.00476 (% for) r = 0.64, f = 1.91
Total nitrogen	
East	Log_{10} (NCONC) = -0.08557 + 0.00716 (% agric + % urb) -0.00227 (% for) r = 0.85, f = 1.51
Central	Log_{10} (NCONC) = -0.01609 + 0.00399 (% agric + % urb) -0.00306 (% for) r = 0.77, f = 1.50
West	Log_{10} (NCONC) = -0.03665 + 0.00425 (% agric + % urb) -0.00376 (% for) r = 0.61, f = 1.75
Inorganic nitrogen	
East	Log_{10} (INCONC) =-0.3479 + 0.00858 (% agric + % urb) -0.00584 (% for) r = 0.84, f = 1.93
Central	Log_{10} (INCONC) = -0.5219 + 0.00482 (% agric + % urb) -0.00572 (% for) r = 0.71,f = 2.06
West	Log_{10} (INCONC) = -0.6339 + 0.00789 (% agric + % urb) -0.00657 (% for) r = 0.65, f = 2.45

From: Omernik (1977)

4.5.4 Nutrient Accounting System

It may be desirable to determine the impact of each nutrient source on the total instream concentration in order to distinguish among the major sources. An accounting procedure utilizing Equations IV-90 and IV-91 can be developed to do this. The following steps outline the procedure.

1. Segment River. Divide the river into major segments. These segment divisions may reflect waste loading distributions or another convenient division scheme chosen at the discretion of the planner. The segments are not necessarily the same as the reaches that have previously been discussed (see Section 4.1). The delineation of reaches as described earlier is based upon lengths of river having uniform hydraulic conditions. Segments, as used here, are purely a convenient subdivision of the river.

2. Quantify and Locate Sources of Nutrients. The quantification of point, nonpoint, and natural sources on the mainstem and tributaries should be accomplished using the best available data. Tabulation can be performed for each different season to reflect the discharge pattern characteristic of each season. The quantification should include total nitrogen and total phosphorus. Tabulate data in terms of average daily input (lb/day). Characterize the location of the nutrient sources by river mile. For nonpoint sources characterize by river mile at both the beginning and end of the source.

3. Perform Mass-Balance. Sum the known sources to determine the total nutrient loading to each segment. Then make the following comparisons:

   a. Compare the total loading with the nutrient input from the mainstem at the upstream end of the segment. This direct comparison permits an assessment of the collective impact of the nutrient sources entering a segment and the upstream contribution of the mainstem.

b. Perform an intersource comparison to ascertain the relative impact of each nutrient source. Express the results for each source as a percent of the total loading.

When a tributary has a high percent contribution steps 1 through 3 can be repeated for the tributary itself to track the sources of the nutrients.

Apply Equations IV-90 and IV-91 to each reach within the segment to determine the instream nutrient concentration throughout the segment. Once this is done this step can be repeated for the next reach.

By applying this analysis one can determine the relative impact of any discharge, determined jointly by the flux of the nutrient and the discharge location. Section 4.1.10 provided a detailed example problem which illustrates the procedure. A brief example also follows.

EXAMPLE IV-14

Computing Total Nitrogen Distribution

This example illustrates the use of Equations IV-90b and IV-91b in calculating the total nitrogen distribution in a river. Suppose the user has been able to estimate the point and nonpoint loading of total nitrogen in a river as shown in Table IV-30.

TABLE IV-30

TOTAL NITROGEN DISTRIBUTION IN A RIVER IN RESPONSE TO POINT AND NON-POINT SOURCE LOADING

Reach Number	River Mile-Point	TN Added* (lbs/day)	TN Cumulative (lbs/day)	Q Cumulative (cfs)	TN Concentration (mg-N/l)
1	0	400 L	400	300	0.25
	9.99	500 D	900	400	0.42
2	10.0	0	900	400	0.42
	14.99	700 D	1,600	600	0.50
3	15.0	800 L	2,400	700	0.64
	20.99	650 D	3,050	900	0.62
4	21.0	0	3,050	900	0.62
	26.0	900 D	3,950	1,000	0.73

* "L" indicates a localized or point source. "D" indicates a diffuse or non-point source whose range of input is over the entire reach.

If these loading rates are estimated over a year, then the flow rates used should also be average annual flows. To compute the concentration at mile 0, Equation IV-90b can be used:

$$TN_o = \frac{(0)(Q_u) + \frac{400}{8.34}}{\frac{300}{1.55}} = 0.25 \text{ mg-N/l}$$

where the following conversions were used:

1 MGD = 1.55 cfs
1 mg/l= 8.34 lb/MG

To determine the concentration at milepoint 9.99, use Equation IV-91b:

$$TN = (0.25)\,\frac{300}{400} + \frac{\frac{500}{8.34}}{\frac{400}{1.55}} = 0.42 \text{ mg-N/l}$$

Note that wx in Equation IV-91 is the 500 lb/day shown in Table IV-30. By reapplying these two basic equations for each reach the user can work downstream through the four reaches. Also note that the total nitrogen concentration has decreased slightly through reach 3, even though more TN has been added. This is because the incoming flow has served to lower the concentration by dilution.

END OF EXAMPLE IV-14

4.6 TOTAL COLIFORM BACTERIA

4.6.1 Introduction

Total coliform bacteria are considered an indicator of the presence of pathogenic organisms, and as such relate to the potential for public health problems. Allowable levels of total coliform bacteria in rivers vary from state to state and according to the water use description characterizing the particular river segment. For example, in Montana (Montana State Dept. of Health and Environmental Sciences, 1973) the raw water supply may not have more than an average of 50 MPN/100 ml* total coliforms if it is to be used as a potable water supply following simple disinfection. In water suitable for bathing, swimming and recreation, as well as growth and marginal propagation of salmonid fishes, an average of 1,000 MPN/100 ml is allowable.

Concentrations of total coliforms vary with the season of the year. Often the heaviest loadings occur during the summer months, but this impact is somewhat offset due to the more rapid die-off at higher temperatures and more intense solar radiation. In the Willamette River (Figure IV-37), for example, the highest counts of 1971-72 were actually observed from November through May (EPA, 1974).

Treated municipal sewage comprises a major source of coliform pollution. Urban stormwater runoff can also be significant, especially

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*MPN means "Most Probable Number". Coliform organisms are not counted individually, but their densities are statistically determined and the results stated as MPN/100 ml.

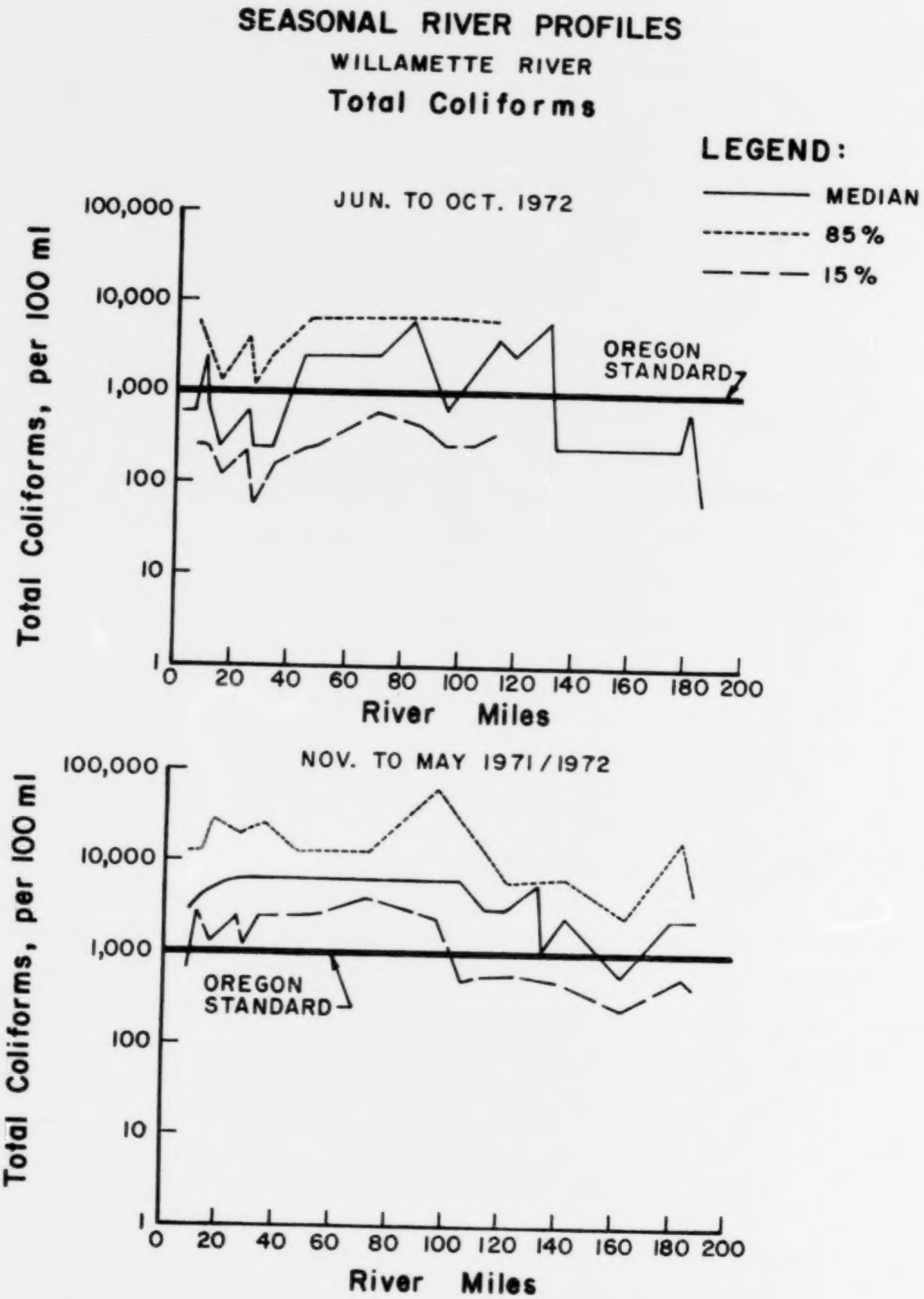


FIGURE IV-37 TOTAL COLIFORM PROFILES FOR THE WILLAMETTE RIVER (EPA, 1974)

through combined sewer outflows. Rural storm water runoff transports significant fecal contamination from livestock pastures, poultry and pig feeding pens, and feedlots. Wildlife both within refuges and in the wilds can contribute as well. For guidance in the interpretation of preliminary coliform analyses, Table IV-31 can be used.

TABLE IV-31

TOTAL COLIFORM ANALYSIS (EPA, 1976)

If the Calculated Concentration is:	Probability of a Coliform Problem
Less than 100/100 ml	Improbable
Less than 1,000/100 ml	Possible
More than 1,000/100 ml	Probable
More than 10,000/100 ml	Highly Probable

4.6.2 Mass Balance for Total Coliforms

The mass balance equations applicable to total coliform organisms are exactly analogous to Equations IV-18, IV-21, and IV-23A and IV-23B, since first order decay is used for both. For purposes of hand computations, the following decay coefficient is acceptable:

$$k_{tc} = 1.0 + 0.02\,(T-20) \qquad \text{(IV-92)}$$

where

k_{tc} = decay coefficient for total coliforms, 1/day
T = water temperature, °C

Those equations with the widest applicability are listed below. For a point source of coliforms:

$$TC = TC_o \exp\left[\frac{-j_{tc}}{A_o}\left(A_o x + \Delta_A \frac{x^2}{2}\right)\right] \qquad \text{(IV-93)}$$

For both point and distributed sources of coliforms:

$$TC = \frac{TC_r}{E_{tc}} + \left(TC_o - \frac{TC_r}{E_{tc}}\right)\left(\frac{Q_o}{Q}\right)^{E_{tc}} \qquad \text{(IV-94)}$$

For a change in coliform concentration due to a point source modification:

$$\Delta TC = \begin{cases} \Delta TC_o \exp\left[\frac{-j_{tc}}{A_o}\left(A_o x + \Delta_A \frac{x^2}{2}\right)\right] & \text{(IV-95a)} \\ \Delta TC_o \left(\frac{Q_o}{Q}\right)^{E_{tc}} & \text{(IV-95b)} \end{cases}$$

where

TC = total coliform concentration, MPN/100 ml

TC_o = initial total coliform concentration, MPN/100 ml

$j_{tc} = \frac{k_{tc}}{U_o}$

TC_r = total coliform level in distributed flow, MPN/100 ml

$E_{tc} = \frac{k_{tc}A_o + \Delta_Q}{\Delta_Q}$

Because of the potential variability in coliform loadings, seasonal analyses may be warranted. Typically the summer months are of primary concern because loadings often increase during this time period and water contact recreation is at its maximum. Major storm events may also be of interest, because of the large coliform loading that may be associated with them.

EXAMPLE IV-15

Estimating the Change in Total Coliform Levels in Response to a Waste Loading Change

Compare the change in total coliform levels, ΔTC, produced by a change ΔTC_o at a given location in a river. Further, determine how this change is affected by a distributed flow entering the river. Relevant data for the river are as follows:

U_o = 1 fps
T = 20°C
Q_o = 500 cfs
Q_f = 800 cfs
x_L = 10 miles
k_{tc} = 1.0/day at 20°C

First the computations will be performed assuming no distributed flow. Equation IV-95A is then applicable. Computing the exponent $j_{tc}x$ (at a flow distance of 10 miles):

$$j_{tc}x = \frac{(1.0)\ (10)\ (5280)}{(24)\ (3600)\ (1)} = 0.611$$

So

$$\frac{\Delta TC}{\Delta TC_o} = \exp\ (-.611) = 0.54$$

or

$$\Delta TC = 0.54\ \Delta TC_o$$

For example if ΔTC_o = -1,000 MPN/100 ml then ΔTC = -540 MPN/100 ml (negative ΔTC_o indicates that the coliform level has decreased from what it previously was).

Now suppose the distributed flow of 300 cfs is included in the computation. Then,

$$E_{tc} = \frac{k_{tc} A_o + \Delta_Q}{\Delta_Q}$$

$$A_o = Q_o/U_o = 500/1 = 500 \text{ ft}^2$$

$$\Delta_Q = \frac{300}{10(5280)} = 0.0057 \text{ ft}^2/\text{sec}$$

$$E_{tc} = \frac{(1.0)\ (500)}{(24)\ (3600)\ (0.0057)}$$

$$= 2.02$$

Then

$$\frac{\Delta TC}{\Delta TC_o} = \left(\frac{500}{800}\right)^{2.02} = 0.39$$

or

$$\Delta TC = 0.39\ \Delta TC_o$$

For $\Delta TC_o = 1{,}000$ MPN/100 ml, $\Delta TC = -390$ MPN/100 ml.

Note that this decrease is 150 MPN/100 ml less than if no distributed flow existed.

To determine the absolute total coliform level, simply add to the original level the resulting change caused by the waste loading modification.

END OF EXAMPLE IV-15

4.7 CONSERVATIVE CONSTITUENTS

4.7.1 Introduction

Conservative constituents are those which are not reactive and remain either in solution or in suspension. They are advected through the water column at the velocity of the river with no loss of mass. The analysis of nutrients, already discussed in this report, was performed assuming they acted conservatively. Other substances, such as salinity, can also be considered as conservative. Chapter 3 contains information on salinity in irrigation return flow for many rivers with salinity problems.

4.7.2 Mass Balance for Conservative Constituents

Two simple mass balance equations are sufficient for analyzing conservative constituents. The first relates the instream concentration due to a point source loading:

$$S = \frac{S_uQ_u + W/5.38}{Q_u + Q_w} \qquad \text{(IV-96)}$$

where

S = resulting pollutant concentration, mg/l
S_u = upstream concentration, mg/l
Q_u = upstream flow rate, cfs
Q_w = point source flow rate, cfs
W = loading rate of pollutants, lb/day

When a distributed flow is present along some length of the river, then the distribution of the conservative pollutant is given by:

$$S = \frac{S_oQ_o}{Q} + \frac{wx}{5.38\,Q} \qquad \text{(IV-97)}$$

where

w = distributed loading rate, lb/day/mi
x = distance downstream, miles

S_0 = initial concentration (at x = 0), mg/l

S in Equation IV-97 is identical with S in Equation IV-93.

EXAMPLE IV-16

Calculating Salinity Distribution in a River

Salinity problems are receiving increased attention in the western United States, particularly relating to the economic issues in the Colorado River Basin and international compacts with Mexico. In the Colorado River high salinity levels in the lower reaches adversely affect nearly twelve million people and approximately one million acres of fertile irrigated farmland (Bessler and Maletic, 1975). The salinity now averages approximately 865 mg/l at Imperial Dam and is projected to be 1,160 mg/l or more by the year 2000, unless firm control actions are taken.

Consider the river shown in Figure IV-38. Predict the salinity distribution based on the inflows and withdrawals shown. Assume the data are averaged over a period of a year. These data, along with the salinity concentrations at different river mileposts are shown in Table IV-32.

To calculate S (salinity at milepoint 100) use Equation IV-96:

$$S = \frac{0.500 + (2\times10^6)(1.55/8.34)}{2000} = 186 \text{ mg/l}$$

At milepost 199.9, Equation IV-97 is appropriate and S is given by:

$$S = \frac{(186)(2000)}{5000} + \frac{(4\times10^6)(1.55/8.34)}{5000} = 223 \text{ mg/l}$$

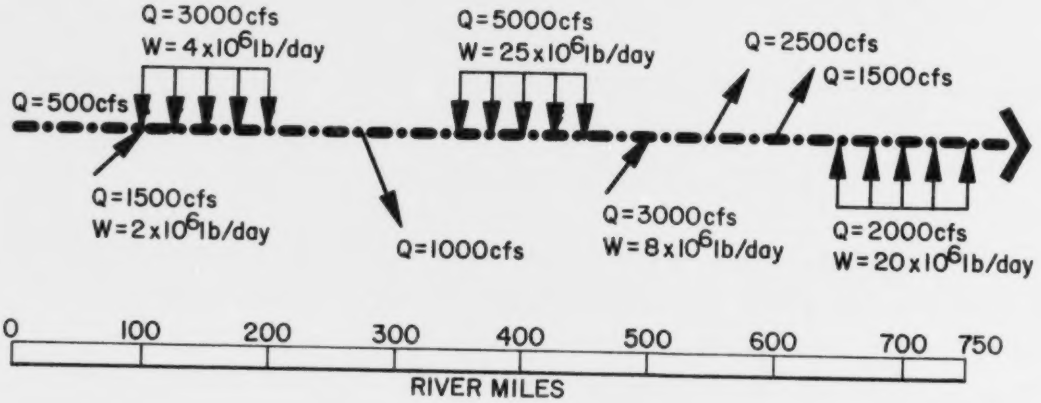

Q=3000cfs
W=4x10⁶lb/day
Q=5000cfs
W=25x10⁶lb/day
Q=2500cfs
Q=1500cfs
Q=500cfs
Q=1500cfs
W=2x10⁶lb/day
Q=1000cfs
Q=3000cfs
W=8x10⁶lb/day
Q=2000cfs
W=20x10⁶lb/day
0
100
200
300
400
500
600
700
750
RIVER MILES

FIGURE IV-38 SALINITY DISTRIBUTION IN A HYPOTHETICAL RIVER

At milepoint 280, 1,000 cfs of flow leaves the mainstem (perhaps for irrigation purposes). The concentration of salinity in this flow is the same as that in the mainstem. So the mass rate of withdrawal is

$$W = \frac{-8.34}{1.55} (223 \times 1000) = -1.2 \times 10^6 \text{ lb/day}$$

A negative sign is used to signify a withdrawal. Completing the remainder of the table is solely a matter of reapplying these basic concepts.

END OF EXAMPLE IV-16

4.8 SEDIMENTATION

4.8.1 Introduction

One of the more difficult classes of hydraulic engineering problems associated with rivers involves the erosion, transportation, and deposition of sediment. Sedimentation is important economically, particularly relating to filling of reservoirs and harbors, and to maintaining channel

TABLE IV-32

SALINITY DISTRIBUTION IN A HYPOTHETICAL RIVER

Reach Number	River Mile Point	Salinity Added* (lbs/day)		Salinity Cumulative (lbs/day)	Q Cumulative (cfs)	Salinity Concentration (mg/l)
1	0	0		0	500	0
	99.9	0		0	500	0
2	100	$2x10^6$	L	$2x10^6$	2000	186
	199.9	$4x10^6$	D	$6x10^6$	5000	223
3	200	0		$6x10^6$	5000	223
	279.9	0		$6x10^6$	5000	223
4	280	$-1.2x10^6$	L	$4.8x10^6$	4000	223
	359.9	0		$4.8x10^6$	4000	223
5	360	0		$4.8x10^6$	4000	223
	449.9	$25x10^6$	D	$29.8x10^6$	9000	615
6	450	0		$29.8x10^6$	9000	615
	499.9	0		$29.8x10^6$	9000	615
7	500	$8\ 10^6$	L	$37.8x10^6$	12000	585
	524.9	0		$37.8x10^6$	12000	585
8	525	$-7.9x10^6$	L	$29.9x10^6$	9500	585
	599.9	0		$29.9x10^6$	9500	585
9	600	$-4.7x10^6$	L	$25.2x10^6$	8000	585
	649.9	0		$25.2x10^6$	8000	585
10	650	0		$25.2x10^6$	8000	585
	750	$20x10^6$	D	$45.2x10^6$	10000	840

*'L' indicates a localized or point source at the milepoint shown in the same row.

'D' indicates a diffuse or non-point source ending at the milepoint shown in the same row and beginning at the milepoint in the above row.

navigability and stability. Table IV-2, located in Section 4.1, documents some suspended solids problems encountered in eight major U.S. waterways.

The sediment load carried in a river can be divided into two components: the bed material load and the wash load. The bed material load is composed of those solid particles represented in the bed. The transport of this material is accomplished both along the bed (bed load) and suspended within the water (suspended load). Although there is no sharp demarcation delineating bed load from suspended load, many researchers have developed individual expressions for each transport component. The total bed material load is the sum of the bed load and the suspended load. Other researchers have developed a unified theory from which the total bed material load can be predicted from a single expression.

The wash load is usually produced through land erosion, rather than channel scour. Wash load is composed of grain sizes finer than found in the bed material. It readily remains in suspension and is washed out of the river without being deposited. A definite relationship between the hydraulic properties of a river and the wash load capacity apparently does not exist, making it difficult to advance an analytical method for washload prediction (Graf, 1971). Not all the erodible material entering a stream is transported as wash load, but a large portion may become part of the bed material and be transported as bed material load.

Figure IV-39 provides a graphical illustration of the difference between wash load and bed material load. For a particular flow condition in a particular river, the river has the capacity to transport a certain quantity of sediment (q_s) which generally decreases as particle size increases. At some large particle size the river cannot exert enough force to transport particles of that size or larger. This situation would occur at some point to the right of point D on curve COD. This same river might be supplied with sediment at a rate AOB, which is unrelated to transport capacity.

To the left of point O the river is transporting all the material of that size range being supplied to it. Sediment having diameters less than d* are classified as wash load, because the amount being transported is

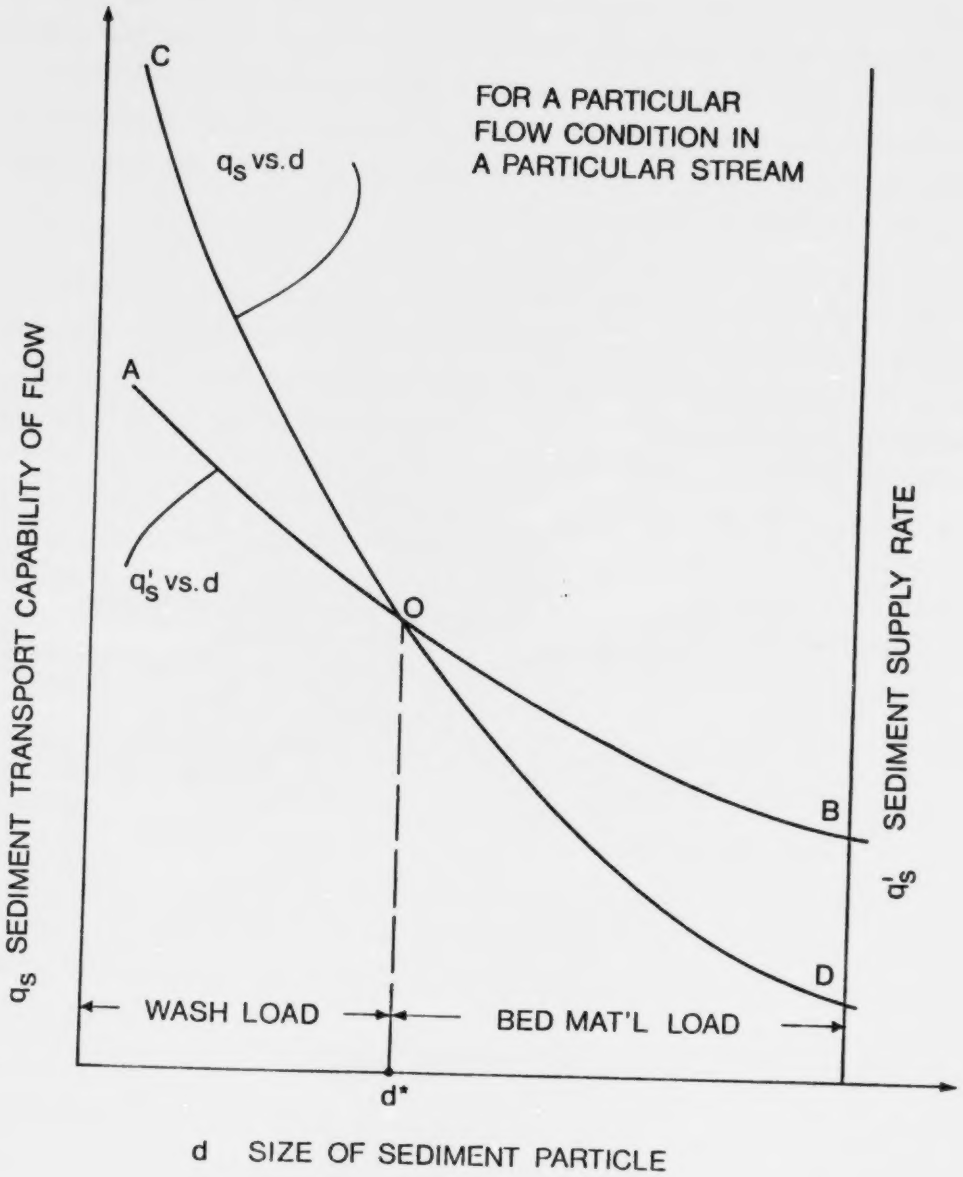

C
q_s vs. d
FOR A PARTICULAR FLOW CONDITION IN A PARTICULAR STREAM
A
q_s' vs. d
O
B
D
q_s SEDIMENT TRANSPORT CAPABILITY OF FLOW
q_s' SEDIMENT SUPPLY RATE
WASH LOAD
BED MAT'L LOAD
d*
d SIZE OF SEDIMENT PARTICLE

FIGURE IV-39 DIVISION BETWEEN WASH LOAD AND BED MATERIAL LOAD (FROM: COLORADO STATE UNIVERSITY, 1979)

supply limited, and not transport limited. To the right of point O, supply exceeds transport capacity. The amount given by the curve OD is transported, and the difference in OB and OD is deposited in the stream bed. The methods to be presented in the following sections are generally concerned with predicting curve OD (i.e. the bed material load), although Section 4.8.2 does provide a brief description of how to estimate long-term sediment supply rates.

As a guide in evaluating whether a river is carrying a significant quantity of suspended sediment, Table IV-33 can be consulted. 100 mg/l is the delineation between a potential and probable problem. In a table previously introduced (Table IV-1), a reference level of 80 mg/l was set for protection of aquatic life.

TABLE IV-33

RELATIONSHIP OF TOTAL SUSPENDED SEDIMENT CONCENTRATION TO PROBLEM POTENTIAL (AFTER EPA, 1976)

If Calculated Concentration is:	Probability of a Problem
Less than 10 mg/l	Improbable
Less than 100 mg/l	Potential
More than 100 mg/l	Probable

4.8.2 Long-Term Sediment Loading from Runoff

The procedures outlined in Chapter 3 will permit an assessment of the sediment loading to a river on a long-term basis. When using those procedures care should be taken to incorporate the entire drainage area of the watershed. As an estimate, the loading can be assumed conservative (i.e. all sediment that comes into the river will be washed out of the river over an extended time period). Under that assumption the procedure outlined in Section 4.7 can be utilized for an estimate of average yearly suspended solids concentrations at locations throughout the river system. This result should be interpreted as an indicator of the impact of the runoff on sediment loads within a river and not as actual suspended solids concentrations. Not all of the incoming sediment will be transported as suspended load since a large fraction can be transported as bed load. The transport process is generally of an intermittent nature with higher concentrations occurring during periods of high flow.

Care should be taken not to apply the conservative assumption at points on a river where that assumption is clearly violated, such as at reservoirs which can be efficient sediment traps. An example for the computation of sediment loading to rivers has been considered in Chapter 3.

4.8.3 Bed Material Load

As previously mentioned, the estimation of bed material transport poses a difficult problem, and is an area where there is no consensus regarding the best predictive relationship to use. Numerous bed material load relationships (Task Committee on Preparation of Sedimentation Manual, 1971) have been developed over the past century, some requiring considerably more input data than others. In this report the DuBoys relationship (Task Committee on Preparation of Sedimentation Manual, 1971) will be used in part because of its simplicity. The relationship, which is restricted to uniform flow in alluvial channels, is:

$$g_b = \Psi\tau_o (\tau_o - \tau_c) \qquad \text{(IV-98)}$$

where

g_b = bed load, lb/sec/ft of width of river

Ψ = coefficient depending on grain size. $ft^3/lb/sec$

τ_o = γR_H S, bed shear stress, lb/ft^2

γ = specific weight of water, lb/ft^3

R_H = river hydraulic radius, ft

S = slope of stream, ft/ft

τ_c = critical shear stress, lb/ft^2

The values of Ψ and τ_c can be expressed as functions of the median size (by weight) of the bed sediment (d_{50}). These relationships are expressed graphically in Figure IV-40. To aid in determining d_{50} Table IV-34 is presented to show the size range of sediment and each associated class name. If the class name of the predominant sediment type comprising a stream bed is known, then the sediment size (in mm) can be estimated. Appendix C also contains d_{50} data for numerous rivers and streams.

Once d_{50} is estimated, then Ψ and τ_c can easily be evaluated, leaving only τ_0 to compute. A summary of hydraulic radii (the ratio of cross-sectional area to wetted perimeter) for different channel

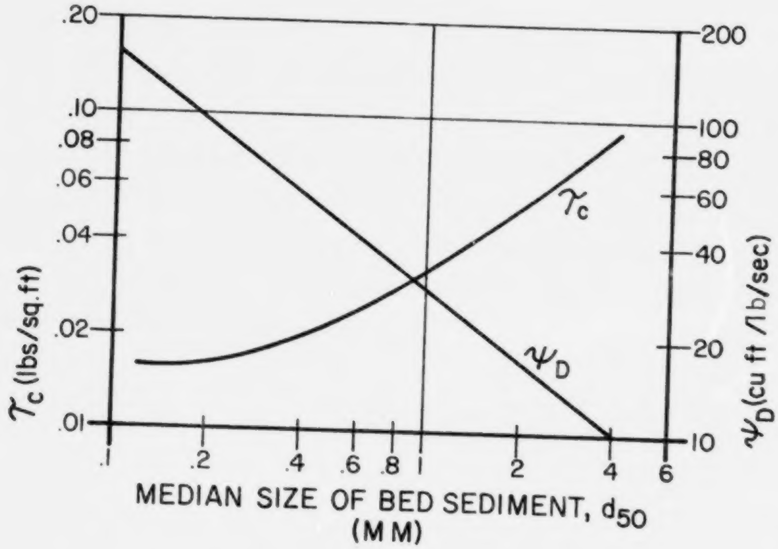


FIGURE IV-40 Ψ AND τ_c FOR DUBOYS RELATIONSHIP AS FUNCTIONS OF MEDIAN SIZE OF BED SEDIMENT (TASK COMMITTEE ON PREPARATION OF SEDIMENTATION MANUAL, 1971)

TABLE IV-34

SEDIMENT GRADE SCALE (TASK COMMITTEE ON PREPARATION OF SEDIMENTATION MANUAL, 1971)

Class Name	Size Range				Approximate Sieve Mesh Openings Per Inch	
	Millimeters		Microns	Inches	Tyler	United States Standard
Very large boulders		4096-2048		160-80		
Large boulders		2048-1024		80-40		
Medium boulders		1024-512		40-20		
Small boulders		512-256		20-10		
Large cobbles		246-128		10-5		
Small cobbles		128-64		5-2.5		
Very coarse gravel		64-32		2.5 -1.3		
Coarse gravel		32-16		1.3 -0.6		
Medium gravel		16-8		0.6 -0.3	2-1/2	
Fine gravel		8-4		0.3 -0.16	5	5
Very fine gravel		4-2		0.16-0.08	9	10
Very coarse sand	2-1	2.000-1.000	2000-1000		16	18
Coarse sand	1-1/2	1.000-0.500	1000-500		32	35
Medium sand	1/2-1/4	0.500-0.250	500-250		60	60
Find sand	1/4-1/8	0.250-0.125	250-125		115	120
Very fine sand	1/8-1/16	0.125-0.062	125-62		250	230
Coarse silt	1/16-1/32	0.062-0.031	62-31			
Medium silt	1/32-1/64	0.031-0.016	31-16			
Fine silt	1/64-1/128	0.016-0.008	16-8			
Very fine silt	1/128-1/256	0.008-0.004	8-4			
Coarse clay	1/256-1/512	0.004-0.0020	4-2			
Medium clay	1/512-1/024	0.0020-0.0010	2-1			
Fine clay	1/1024-1/2048	0.0010-0.0005	1-0.5			
Very fine clay	1/2048-1/4096	0.0005-0.00024	0.5-0.24			

geometries is shown in Figure IV-41. For very wide, shallow channels, the hydraulic radius approximately equals the depth of flow. Many river cross-sections can be approximated by a parabolic section. To calculate "c" in the relationship for hydraulic radius of a parabolic section, refer to Table IV-35.

If the bed slope is unknown it can be estimated by using a topographic map and finding contour lines approximately five hundred feet above and below the point on the river where the measurement is to be made. Dividing this elevation difference by the horizontal distance over which the difference is measured, produces the slope.

TABLE IV-35

COMPUTING D/T FOR DETERMINING THE HYDRAULIC RADIUS OF A PARABOLIC SECTION (FROM KING, 1954)

$\frac{D}{T}^*$	.00	.01	.02	.03	.04	.05	.06	.07	.08	.09
.0	.667	.667	.666	.665	.664	.662	.660	.658	.656	.653
.1	.650	.646	.643	.639	.635	.631	.626	.622	.617	.612
.2	.607	.602	.597	.592	.586	.581	.575	.570	.564	.559
.3	.554	.548	.543	.537	.532	.526	.521	.516	.510	.505
.4	.500	.495	.490	.485	.480	.475	.470	.465	.460	.455
.5	.451	.446	.442	.437	.433	.428	.424	.420	.416	.412
.6	.408	.404	.400	.396	.392	.388	.385	.381	.377	.374
.7	.370	.367	.364	.360	.357	.354	.351	.348	.344	.341
.8	.338	.335	.333	.330	.327	.324	.321	.319	.316	.313
.9	.311	.308	.306	.303	.301	.298	.296	.294	.291	.289

$^*\frac{D}{T} = c$

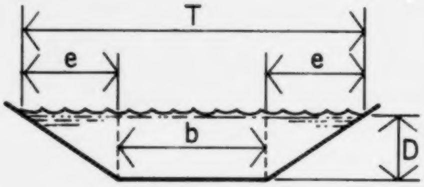
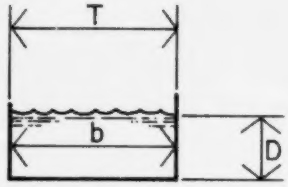
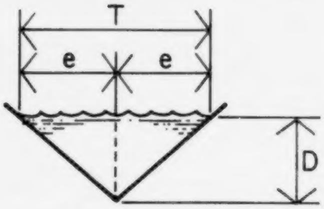
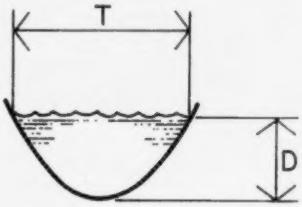
CHANNEL SLOPE	HYDRAULIC RADIUS
 Trapezoidal	$\frac{(1 + zx)\,D}{1 + 2x\sqrt{1 + x^2}}$, $x = D/b$, $z = e/D$
 Rectangular	$\frac{bD}{b + 2D}$
 Triangular	$\frac{zD}{2\sqrt{1 + z^2}}$ $z = e/D$
 Parabolic	cD (for c, see Table IV-29)

Figure IV-41 Hydraulic Radii for Different Channel Shapes (from King, 1954)

Adequate methods that are within the scope of this report and which would provide a straightforward estimation of suspended sediment discharge presently do not exist. Most relationships require a known reference level concentration at some depth within the river to predict the concentration at another depth (Morris and Wiggert, 1972). To determine the suspended sediment load, then, a summation of contributions at each depth must be made. Since these formulas apply to one grain size this procedure should be repeated for all grain sizes present. Einstein (Graf, 1971) has developed a method for computing suspended sediment discharge that does not require knowledge of a reference concentration, but it is an advanced approach. For this report the contribution of the suspended load will be estimated from the bed material load by the relationship given in Table IV-36. The relationship in Table IV-36 is valid for graded channels (by graded is meant that the slope is stable over time, being neither steepened nor flattened by flow or other influence).

TABLE IV-36

RELATIONSHIP BETWEEN WIDTH TO DEPTH RATIO OF A GRADED STREAM AND THE SUSPENDED AND BED LOAD DISCHARGE (AFTER FENWICK, 1969)

Suspended Load % of Total Bed Material Load	Bed Load % of Total Bed Material Load	Width-Depth Ratio
85-100	0-15	7
65-85	15-35	7-25
30-65	35-70	25

Once the width to depth ratio for the stream in question is determined, the suspended load can then be approximated after first computing the bed material load, and then using Table IV-36.

Once the suspended load discharge is estimated the average concentration at a section can be computed by:

$$C_{ss} = \frac{G_{ss}}{Q} 1.6 \times 10^4 \qquad \text{(IV-99a)}$$

or

$$C_{ss} = \frac{g_{ss}}{q} 1.6 \times 10^4 \qquad \text{(IV-99b)}$$

where

C_{ss} = average suspended solids concentration, mg/l

G_{ss} = suspended solids discharge, lb/sec

Q = flow rate, cfs

g_{ss} = suspended solids discharge per unit width, lb/sec/ft

q = flow rate per unit width, cfs/ft

The procedures discussed in this section can be summarized as follows:

1. Determine the bed load discharge g_b (lb/sec/ft) using Equation IV-98. The required input data are channel slope, hydraulic radius (see Figure IV-41), and the median sediment size, d_{50} (see Appendix C). Once d_{50} has been estimated the unknown parameters τ_c and Ψ can be found from Figure IV-40.

2. Multiply g_b by the river width to find the total bed load discharge.

3. Determine the width/depth ratio.

4. Use Table IV-36 to determine the suspended load.

5. To determine the suspended sediment concentration use Equation IV-99.

6. Compare the suspended sediment concentration against the data in Table IV-33 to find out if a problem potentially exists.

7. The total bed material load is sum of the total bed load (step 2) and the total suspended load (step 4).

The user may be primarily concerned with the total bed material load rather than either bed load or suspended load individually. Total bed material load can be directly calculated using a number of predictive formulas. The method of Yang (1976) based on unit stream power is presented here. Yang's method has been verified for the following parameter ranges:

- median bed size from 0.16 mm to 1.0 mm
- channel depth 0.2 ft to 49.9 ft
- water temperature from 0^{o}C to 29.4^{o}C
- stream velocity from 1.23 fps to 7.82 fps
- flow rate from 2.7 cfs to 470,000 cfs
- slope from 0.0000428 to 0.00188
- total sediment concentration (excluding wash load) from 2.8 ppm to 2,440 ppm

The input data are the same as for the DuBoy's method, with the addition of water temperature. The predictive formula, however, is considerably more complicated, so the method has been programmed on a hand held calculator and the program is included. The predictive expression is:

$$\log C_t = 5.435 - 0.286 \log \frac{wD}{\nu} - 0.457 \log \frac{U_*}{w}$$
$$+ (1.799 - 0.409 \log \frac{wD}{\nu} - 0.314 \log \frac{U_*}{w}) \log (\frac{US}{w} - \frac{U_{cr}S}{w}) \quad \text{(IV-100)}$$

where

C_t = total sediment concentration in parts per million by weight
D = median sieve diameter
S = water surface slope or energy slope
U_* = shear velocity
U = average water velocity
U_{cr} = critical average water velocity at incipient motion

ν = kinematic viscosity
w = terminal fall velocity

The term $\frac{U_{cr}}{w}$ can be calculated as

$$\frac{U_{cr}}{w} = \frac{2.5}{\log(\frac{U_* D}{\nu}) - 0.06} + 0.66 \text{ when } 1.2 < \frac{U_* D}{\nu} < 70 \qquad \text{(IV-101)}$$

and

$$\frac{U_{cr}}{w} = 2.05 \text{ when } 70 \leq \frac{U_* D}{\nu} \qquad \text{(IV-102)}$$

Figure IV-42 shows the required user instructions to execute the program on a TI-59. Figure IV-43 contains the program listing and a sample input/output. This program was written by Colorado State University (1979).

EXAMPLE IV-17

Estimation of Bed Material Load

Table IV-37 shows characteristics of the Colorado River at Taylor's Ferry, California, and of the Niobrara River near Cody, Nebraska. Suppose one desires to calculate the bed load for the Colorado River at this location for flow ranges of 8-35 cfs/ft. The following data will be used:

d_{50} = 0.33 mm
γ = 62.4 lb/ft^3, at 60^{o}F
S = 0.000217 ft/ft

Using Figure IV-40 one finds

Ψ = 64
τ_c = 0.019

TITLE ____________ PAGE 1 OF 1

PROGRAMMER ____________ DATE ____________

Partitioning (Op 17) 4, 6, 0 6, 0 Library Module ____________ Printer Optional Cards 1

PROGRAM DESCRIPTION

Program: Yang's Sediment Transport Equation

USER INSTRUCTIONS

STEP	PROCEDURE	ENTER	PRESS			DISPLAY
1	Enter kinematic viscosity, $\nu\left(\frac{ft^2}{sec}\right)$	ν	A			ν
2	Enter slope S_o (ft/ft)	S_o	B			S_o
3	Enter median sediment diameter, d_s (ft)	d_s	C			d_s
4	Enter flow velocity, U $(\frac{ft}{sec})$	U	D			U
5	Enter flow depth, Y (ft)	Y	E			Y
6	Compute sediment concentration (ppm)		2nd	A'		C_t
7	To input new data, repeat steps 1 through 6.					

FIGURE IV-42 USER INSTRUCTIONS FOR YANG'S SEDIMENT TRANSPORT EQUATION.

Program Listing:

```
000  76 LBL
001  77   GE
002  93   .
003  00   0
004  00   0
005  00   0
006  02   2
007  32 X:T
008  43 RCL
009  02   02
010  77   GE
011  88 DMS
012  33 X²
013  65   ×
014  02   2
015  93   .
016  09   9
017  05   5
018  01   1
019  07   7
020  55   ÷
021  43 RCL
022  06   06
023  95   =
024  42 STO
025  00   00
026  92 RTN
027  76 LBL
028  88 DMS
029  53   (
030  53   (
031  53   (
032  43 RCL
033  02   02
034  45 Yˣ
035  03   3
036  65   ×
037  03   3
038  06   6
039  93   .
040  00   0
041  06   6
042  04   4
043  85   +
044  03   3
045  06   6
046  65   ×
047  43 RCL
048  06   06
049  33 X²
050  54   )
```

```
051  34 √X
052  75   -
053  06   6
054  65   ×
055  43 RCL
056  06   06
057  54   )
058  55   ÷
059  43 RCL
060  02   02
061  54   )
062  42 STO
063  00   00
064  92 RTN
065  76 LBL
066  11   A
067  42 STO
068  06   06
069  22 INV
070  52 EE
071  92 RTN
072  76 LBL
073  12   B
074  42 STO
075  01   01
076  92 RTN
077  76 LBL
078  13   C
079  42 STO
080  02   02
081  92 RTN
082  76 LBL
083  14   D
084  42 STO
085  03   03
086  92 RTN
087  76 LBL
088  15   E
089  42 STO
090  04   04
091  92 RTN
092  76 LBL
093  16   A'
094  71 SBR
095  77   GE
096  53   (
097  53   (
098  03   3
099  02   2
100  93   .
```

```
101  02   2
102  65   ×
103  43 RCL
104  04   04
105  65   ×
106  43 RCL
107  01   01
108  54   )
109  34 √X
110  42 STO
111  05   05
112  65   ×
113  43 RCL
114  02   02
115  55   ÷
116  43 RCL
117  06   06
118  54   )
119  42 STO
120  07   07
121  32 X:T
122  07   7
123  00   0
124  32 X:T
125  77   GE
126  89   π
127  53   (
128  53   (
129  02   2
130  93   .
131  05   5
132  55   ÷
133  53   (
134  43 RCL
135  07   07
136  28 LOG
137  75   -
138  93   .
139  00   0
140  06   6
141  54   )
142  54   )
143  85   +
144  93   .
145  06   6
146  06   6
147  54   )
148  42 STO
149  08   08
150  61 GTO
```

```
151  70 RAD
152  76 LBL
153  89   π
154  02   2
155  93   .
156  00   0
157  05   5
158  42 STO
159  08   08
160  76 LBL
161  70 RAD
162  53   (
163  53   (
164  05   5
165  93   .
166  04   4
167  03   3
168  05   5
169  75   -
170  93   .
171  02   2
172  08   8
173  06   6
174  65   ×
175  53   (
176  43 RCL
177  00   00
178  65   ×
179  43 RCL
180  02   02
181  55   ÷
182  43 RCL
183  06   06
184  54   )
185  28 LOG
186  42 STO
187  09   09
188  75   -
189  93   .
190  04   4
191  05   5
192  07   7
193  65   ×
194  53   (
195  43 RCL
196  05   05
197  55   ÷
198  43 RCL
199  00   00
200  54   )
```

FIGURE IV-43 PROGRAM LISTING AND SAMPLE INPUT/OUTPUT FOR YANG'S SEDIMENT TRANSPORT EQUATION

Program Listing (continued):

```
201   28 LOG      251   28 LOG
202   42 STO      252   98 ADV
203   10  10      253   99 PRT
204   54  )       254   92 RTN
205   85  +
206   53  (
207   53  (
208   01  1
209   93  .
210   07  7
211   09  9
212   09  9
213   75  -
214   93  .
215   04  4
216   00  0
217   09  9
218   65  ×
219   43 RCL
220   09  09
221   75  -
222   93  .
223   03  3
224   01  1
225   04  4
226   65  ×
227   43 RCL
228   10  10
229   54  )
230   65  ×
231   53  (
232   43 RCL
233   03  03
234   65  ×
235   43 RCL
236   01  01
237   55  ÷
238   43 RCL
239   00  00
240   75  -
241   43 RCL
242   08  08
243   65  ×
244   43 RCL
245   01  01
246   54  )
247   28 LOG
248   54  )
249   54  )
250   22 INV
```

Sample Input:

ν = .0000111

S_o = .0017

d_s = .000623

U = 2.89

Y = 0.51

Output:

C_t = 2117.066395

FIGURE IV-43 (CONTINUED)

TABLE IV-37

CHARACTERISTICS OF THE COLORADO AND NIOBRARA RIVERS (TASK COMMITTEE ON PREPARATION OF SEDIMENTATION MANUAL, 1971)

Data	Stream	
	Colorado River (Taylor's Ferry)	Niobrara River (Cody, Neb.)
Depth range, ft	4-12	0.7-1.3
Range in q, in cubic feet per second per foot of width	8-35	1.7-5
Mean width, in feet	350	110
Slope, in feet per foot		
Minimum value	0.000147	0.00116
Maximum value	0.000333	0.00126
Value used in calculations	0.000217	0.00129
Water temperature, in degrees Fahrenheit		
Minimum value	48	33
Maximum value	81	86
Value used in calculations	60	60
Geometric mean*sediment size, in millimeters	0.320	0.283
d_{35}, in millimeters	0.287	0.233
d_{50}, in millimeters	0.330	0.277
d_{65}, in millimeters	0.378	0.335
d_{90}, in millimeters	0.530	0.530
Mean size, d_m, in millimeters	0.396	0.342

*The geometric mean of a set of values X_n is $\left(\prod_{i=1}^{n} X_n\right)^{1/n}$. Thus the geometric mean of the values 1, 2, 3, and 4 is $(1\times2\times3\times4)^{1/4} = 2.213$. Compare with arithmetic mean of 2.5.

All that remains is the computation of the hydraulic radius. Since the width is much greater than the depth, assume $R_H = D$.

$$R_H = \begin{cases} 4 \text{ ft at } q = 8 \text{ cfs/ft} \\ 12 \text{ ft at } q = 35 \text{ cfs/ft} \end{cases}$$

Using Equation IV-98 it is found that the bed load is

$$g_b = \begin{cases} 0.12 \text{ lb/sec/ft at } q = 8 \text{ cfs/ft} \\ 1.5 \text{ lb/sec/ft at } q = 35 \text{ cfs/ft} \end{cases}$$

The actual bed material load observed at Taylor's Ferry has been compared with the DuBoys prediction for a range of flow rates (Task Committee on Preparation of Sedimentation Manual, 1971). This relationship is shown in Figure IV-44 (The DuBoys curve in Figure IV-44 does not quite match the calculations in this example because slightly different data were used). Observe that the DuBoys relationship overpredicts the bed material load for nearly all flow ranges. This pattern is repeated for the Niobrara River (Figure IV-45). This suggests that the bed material load estimated by the DuBoys relationship will in general exceed the actual bed material load. This is further substantiated by other work (Stall et al., 1958). The more accurate predictions of bed material load occur under high flow conditions, which is generally when the prediction of bed material load is most important.

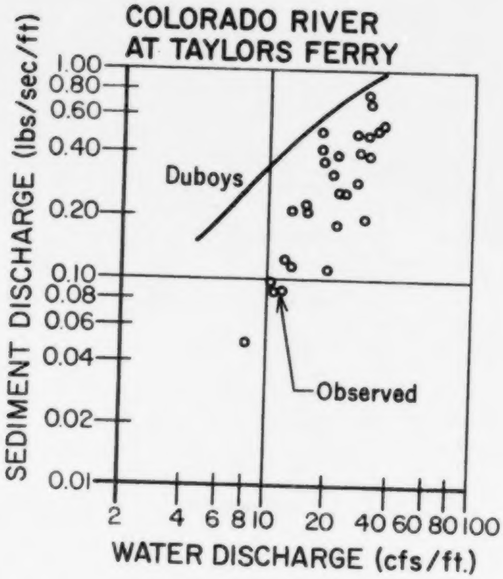


FIGURE IV-44 SEDIMENT DISCHARGE AS A FUNCTION OF WATER DISCHARGE FOR THE COLORADO RIVER AT TAYLOR'S FERRY (TASK COMMITTEE ON PREPARATION OF SEDIMENTATION MANUAL, 1971)

To estimate the suspended load contribution first calculate the width-depth ratio:

$$W/D = \begin{cases} 88 \text{ at } q = 8 \text{ cfs/ft} \\ 29 \text{ at } q = 35 \text{ cfs/ft} \end{cases}$$

In both cases W/D >25. Referring to Table IV-36, the suspended load should be between 30 and 65 percent of the bed material load. Assume it is on the lower end of the scale, about 40%. Then the suspended load is

$$g_{ss} = \begin{cases} 0.08 \text{ lb/sec/ft at } q = 8 \text{ cfs/ft} \\ 1.0 \text{ lb/sec/ft at } q = 35 \text{ cfs/ft} \end{cases}$$

or

$$C_{ss} = \begin{cases} 160 \text{ mg/l at } q = 8 \text{ cfs/ft} \\ 440 \text{ mg/l at } q = 35 \text{ cfs/ft} \end{cases}$$

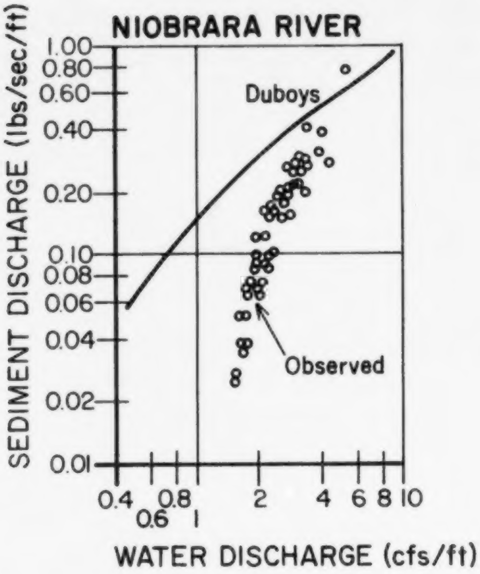


FIGURE IV-45 SEDIMENT DISCHARGE AS A FUNCTION OF WATER DISCHARGE FOR THE NIOBRARA RIVER AT CODY, NEBRASKA (TASK COMMITTEE ON PREPARATION OF SEDIMENTATION MANUAL, 1971)

from Equation IV-99. These concentrations indicate that suspended sediment concentrations are excessively high throughout the range of flows normally encountered at Taylor's Ferry. Data on suspended sediment concentrations have been gathered at Taylor's Ferry (U.S. Bureau of Reclamation, 1958). The averages of 30 measurements taken there are as follows:

$Q = 7350$ cfs (or $q = 21$ cfs/ft)

$C_{ss} = 132$ mg/l

Observed range of suspended sediment
concentration: 40-277 mg/l

The method of Yang predicts total concentrations of 40 to 80 mg/l, which is within but toward the lower end of the observated data. The method of DuBoy's predicts concentration between 160 and 440 mg/l which is toward, and beyond, the upper end of observation. These results illustrate the possible variability of predictions between different approaches, and are not necessarily atypical.

END OF EXAMPLE IV-17

4.9 TOXIC SUBSTANCES

4.9.1 Methods of Entry of Toxic Pollutants into Rivers

Although Chapter 3 discussed both point and nonpoint sources of pollutants, the major pollutant source categories are summarized in Table IV-38 to indicate how these scenarios differentially govern a pollutant's fate. For simplicity, fate is analyzed in terms of volatilization and sorption since these processes are important for a wide number of toxic organic chemicals. These processes govern whether a pollutant remains in the water column and whether the pollutant is transported as solute or sorbate. If the effects of these processes are known, even if only qualitatively, then the influence of processes such as photolysis and biodegradation can be better predicted. For example, if a pollutant is sorbed to suspended and bedded sediments, it is more protected from photolytic reactions than when it is dissolved in the water column.

A common mode of pollutant entry is by a continuous discharge, either from a municipal or industrial source. As mixing of the effluent and river water occurs, partitioning begins. The sorbate is transported with the

TABLE IV-38

METHODS OF INTRODUCTION OF TOXIC ORGANIC COMPOUNDS INTO RIVERS, AND FATE IN TERMS OF VOLATILIZATION AND SORPTION

Pathway	Fate
Continuous input	- solute transported and volatilized - sorbate transported with suspended solids and with bed load - sorbed to immobile sediments - buried by sorption and net deposition
Cessation of continuous input	- desorbed from immobile sediments - solute transported and volatilized - resorbed to suspended sediments - contaminated sediments resuspended - portion remains buried
Washoff from land application	- transport of a major portion of pollutant may be governed by first large storm event - transported as solute and sorbate - settles and accumulates on bed - buried - subsequently resuspended
Accidental releases (e.g. spills)	- If s.g. >1, pollutant settles on streambed - Volatilization may be unimportant --reentrained back into stream and sorbed on suspended solids --pollutant can be slowly transported along bottom --diffused into bedded sediments - If s.g. <1, pollutant tends to remain on surface and be transported at speed of surface current --volatilization can be important --gradually dissolved and sorbed --dispersion attenuates peak concentrations --wind speed and direction influential
Leaching	- slow movement (years) of solute from dump or disposal site to stream - continues for years after cleanup of dump

suspended sediments, and can interact with the bed load and immobile bedded sediments. Depending on the rate of exchange of the sorbate with the bedded sediments and on the net sediment deposition rate, some of the sorbate can gradually become buried in the bedded sediments.

If a continuous input ceases, the water column initially tends to clean itself of the pollutant as uncontaminated upstream water replaces contaminated river water downstream from the former source of pollution. However, pollutant from the contaminated bottom sediments can desorb back into the water column at low concentrations and the river bed becomes an internal source of pollutant. The desorption period can last a long period of time, depending on the amount of pollutant contained in the bottom sediments. Section 4.9.3.4 discusses this phenomenon in detail.

Periodic nonpoint sources, such as washoff after an agricultural application, is another pathway of pollutant entry into rivers. The mass of pollutant transported tends to be governed by the timing of the first storm event following application together with the degradation and volatilization processes operative during the interim period.

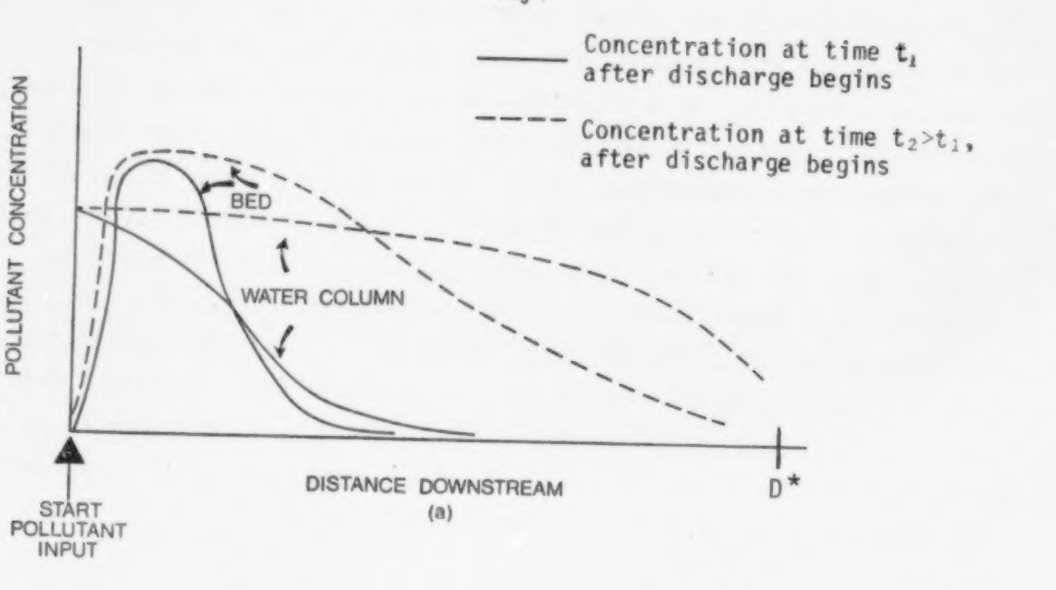
Accidental releases of pollutants, even through infrequent events, can be important. Exceptionally high concentrations of pollutants can result from spills and the total mass supplied almost instantaneously can be the equivalent of a continuous release lasting for many days. For example, in 1973 a chloroform spill on the Mississippi River resulted in about 800,000 kg (1,750,000 lbs) of chloroform being released over a period of several hours (Thibodeaux, 1977). Based on the background concentration of chloroform in the river (5 ppb), the release was equivalent to a continuous supply of chloroform released at background rates for a period of 300 days.

Many chemicals in their pure or nearly pure form have specific gravities significantly different from unity. Because of this, and their often limited solubility in water, it is a mistake to believe that all spilled pollutants travel with the speed of the river, have infinite dissolution capability, and disperse accordingly. High density pollutants can sink to the river bed and become slowly reentrained back into the water column while simultaneously diffusing and sorbing into the bedded sediments. Depending on the rate of dissolution of the spilled pollutant, as well as the significance of the sorption and diffusion processes, the spilled pollutant may remain in the riverine system for either an extended or brief period of time.

In contrast to high density pollutants, pollutants with specific gravities less than unity tend to at least partially remain on or near the water's surface while undergoing dissolution. For these pollutants, volatilization and photolysis can be extremely important. As the pollutant is dissolved in the water column and moves downstream, dispersion becomes important in attenuating the peak concentration.

Pollutants which leach from a surface or subsurface disposal site may eventually reach a river. Although the mass input rate may be low, the source can be continuous and last for years, even after cleanup of the site.

The sequence of instream events following the initiation and then the cessation of point sources of toxicants further illustrates the role that sorption plays in governing fate of sorbates. Figure IV-46 illustrates the two situations. Figure IV-46a shows the pollutant distributions below a point source at two distinct times (t_1 and t_2 where $t_2 > t_1$) following initiation of the point source. As the toxicant is discharged the water column concentration (the sum of the dissolved and sorbed phases) abruptly increases at the mixing location. As the pollutant travels downstream, the sorbate tends to partially desorb onto the formerly uncontaminated bottom sediments. Additionally there may be a net exchange between the bedded sediments and water column sediments, even if there is no net deposition. As a result of these processes, the water column concentration tends to decrease in the downstream direction. It may take a period of time greater than t_1 for the effects of the discharge to reach a distance D*. Depending on the distance, and on the rate of accumulation of the toxicant in the bottom sediments, as well as on other factors, the time required for the water column concentration to be noticeably elevated at D* could greatly exceed the travel time of the river over the distance.



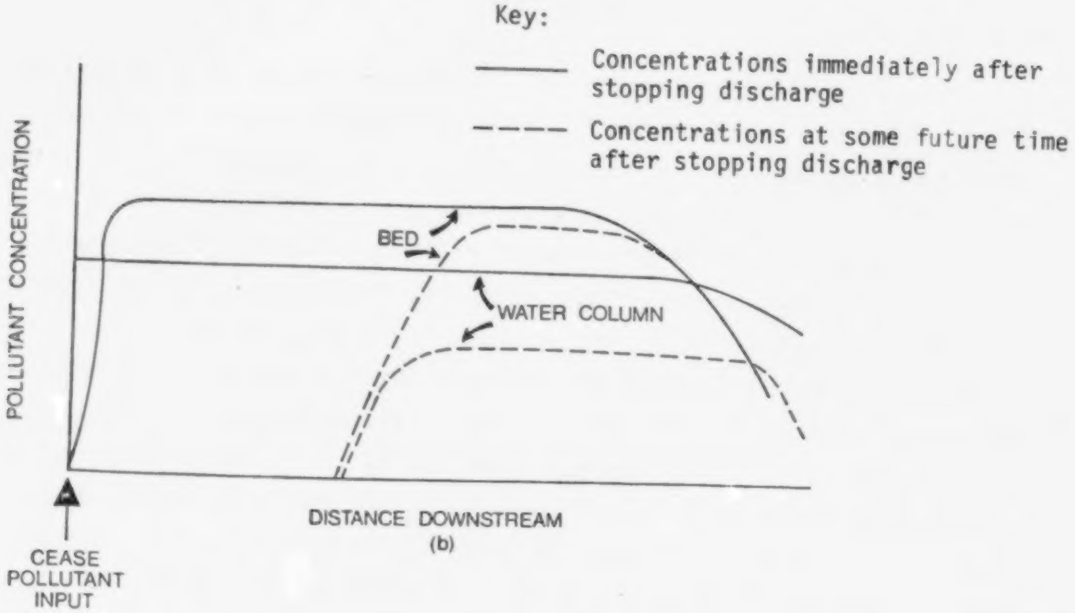


FIGURE IV-46 TOXICANT CONCENTRATIONS FOLLOWING INITIATION AND CESSATION OF POINT SOURCE.

After the discharge of the toxicant has continued for a period of time, the net exchange with the bedded sediment may diminish, so that the toxicant concentration becomes constant over some distance both in the water column and in the sediments. This situation is illustrated by the solid curve in Figure IV-46b. Suppose at this time the input of the pollutant ceases. The water column concentration just below the point source tends to abruptly approach zero. As this happens, desorption of the toxicant from the bedded sediment can occur, tending to replenish pollutant levels in the water column, but to a lower level. Gradually, the pollutant can be desorbed from the bedded sediments at a given location so that the bottom sediments are naturally cleansed, from the upstream to the downstream direction. This process can take many years and low levels of pollutant in the water column can be detected throughout this period. More discussion of this phenomenon is provided later in Section 4.9.3 and Example IV-18.

4.9.2 Vertical Distribution of Sorbate within Rivers

Even though most of the analytical tools presented later in Section 4.9.3 assume that, for simplicity, suspended solids concentrations are uniformly distributed throughout the water column, in reality this is not true. The vertical distribution of solids depends both on particle and river characteristics. Heavier particles (those with the greater settling velocities) are transported closer to the stream bottom while the lighter particles are more uniformly distributed. This observation is significant because pollutants which sorb to the particles also exhibit a non-uniform vertical distribution. Pollutants which do not sorb tend to become uniformly distributed vertically, regardless of the sediment distribution. By understanding this, the user can better interpret instream pollutant data, particularly if the pollutant tends to reside as sorbate. It may be that a single pollutant sample is not sufficient to accurately characterize the pollutant distribution, and in fact could be misleading in terms of the total burden of the pollutant carried within the water column. Depth integrated samples might be necessary to gain an accurate knowledge of the pollutant's distribution.

Figure IV-47 shows the vertical distribution of suspended solids in an equilibrium condition. The parameter shown in the figure is defined:

$$z = \frac{V_s}{\kappa U^*} \tag{IV-103}$$

where

V_s = settling velocity of suspended solids
κ = von Karman's constant ($\sim$0.4)
U^* = shear velocity = $(g R_H S)^{0.5}$, ft/sec
g = acceleration due to gravity, 32.2 ft/sec^2
R_H = hydraulic radius of river, ft
S = slope, dimensionless.

Very small values of z represent clay-sized particles, while larger values represent first silt, and then sand. Figure IV-47 illustrates that clay particles tend to be uniformly distributed vertically (50 percent in the top half of the water column). About 75 percent of silt and over 95 percent of the sand particles (typically) reside in the bottom half of the water column. This suggests that in rivers where the suspended sediments are silt and sand, the sorbed pollutant distribution will be vertically skewed. If the suspended material is predominantly clay the sorbed pollutant distribution will be uniform. Since pollutants tend to sorb to sand to a lesser degree than to silt and clay, the vertical distribution of sorbed pollutant will not be as skewed as the suspended sediment distribution.

Figures IV-48 through IV-49 show the fraction of pollutant present as solute (C/C_t) versus relative depth for families of z values and K_pSa values. Sa is the suspended sediment concentration a small distance above the bottom. For K_pSa values less than 0.1, the sorbate concentration is generally negligible compared to the solute concentration regardless of the depth or the nature of the suspended material. For larger K_pSa values, the sorbate level can be important, depending of the nature of the suspended material. For extremely large K_pSa values, the sorbate concentration will greatly exceed the solute concentration, at least near the river bed.

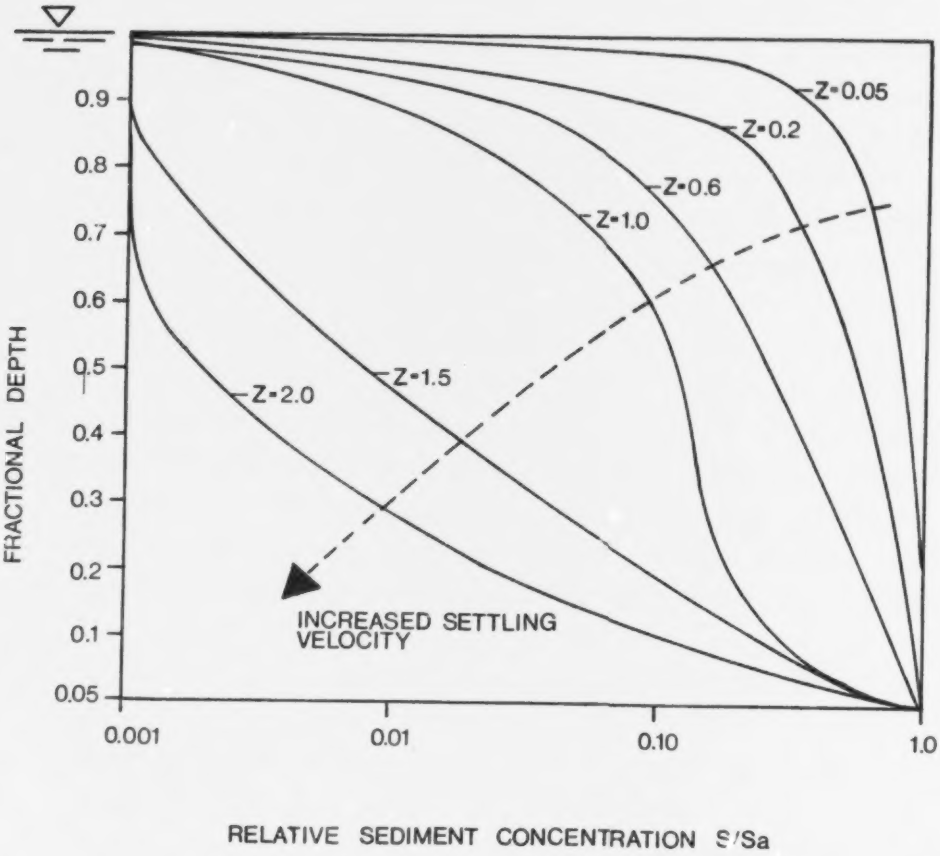


FIGURE IV-47 VERTICAL EQUILIBRIUM DISTRIBUTION OF SUSPENDED SOLIDS IN A RIVER

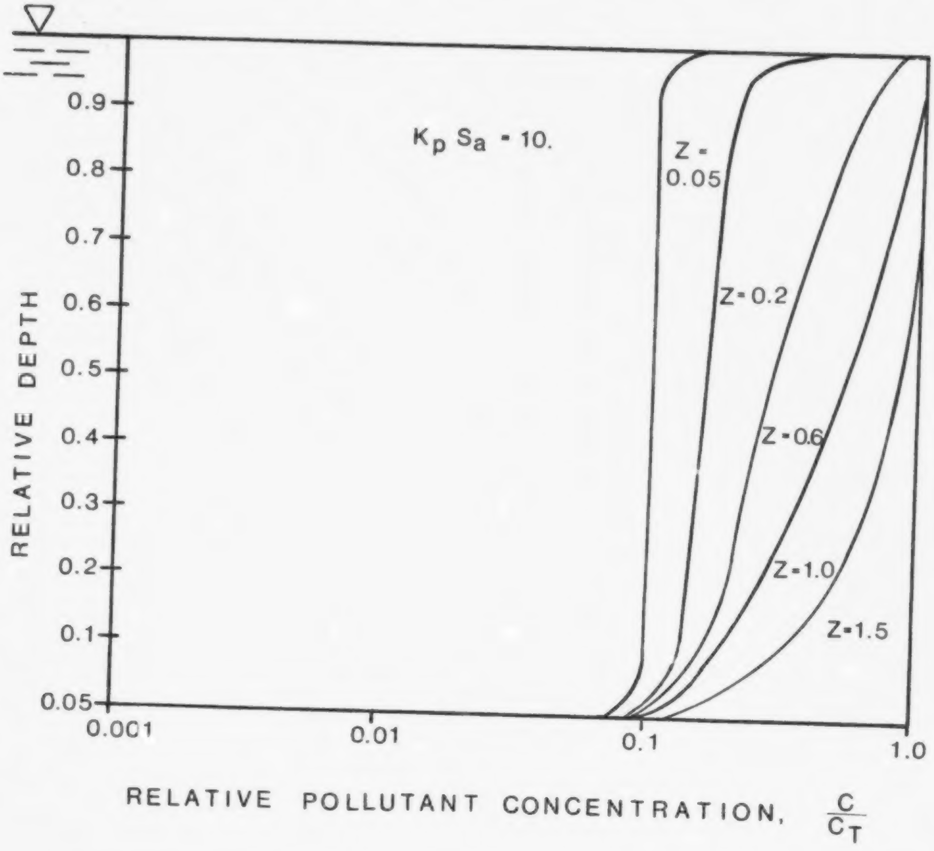


FIGURE IV-48 VERTICAL DISTRIBUTION OF RELATIVE SOLUTE CONCENTRATION, $K_P S_A = 10$.

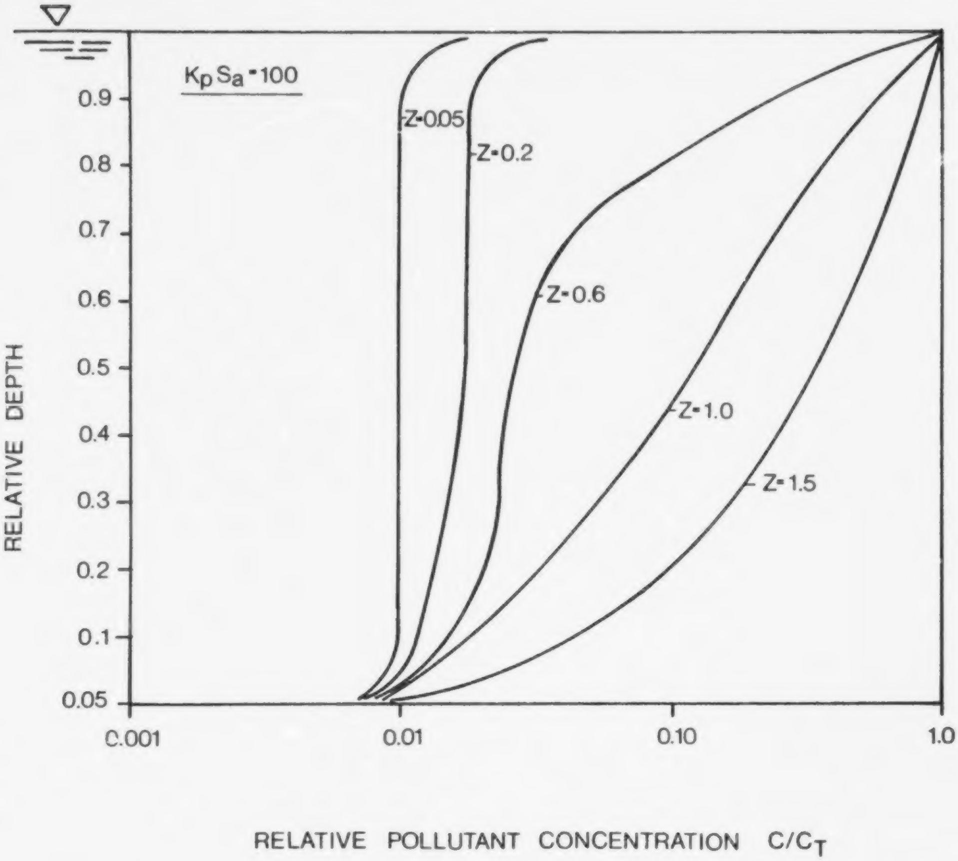


FIGURE IV-49 VERTICAL DISTRIBUTION OF RELATIVE SOLUTE CONCENTRATION, $K_PS_A = 100$.

Based on the hydraulic characteristics of the river, characteristics of the material being transported in suspension, and the partition coefficient of the pollutant, predictions can be made of the pollutant's distribution in the water column. To use Figures IV-48 and IV-49 requires knowledge of Sa, the suspended solids concentration at a distance n = a above the bottom (where typically a = 0.05, or 5 percent of the river's depth). The equilibrium expression for suspended sediments, which is found in numerous sediment transport texts (e.g. Graf, 1971) can be rearranged to express Sa as:

$$Sa = S(n)\left(\frac{1-n}{n}\ \frac{a}{1-a}\right)^{-z} \qquad \text{(IV-104)}$$

where

n = relative depth above bottom

To use this equation the suspended solids concentration must be known at one depth in the water column. Typically, a depth averaged suspended solids concentration might be readily available. Under these circumstances Sa can be estimated as:

$$Sa = \frac{S\left(1-a\right)\left(\frac{1-a}{a}\right)^{z}}{\int_{a}^{1}\left(\frac{1-n}{n}\right)^{z} dn} \qquad \text{(IV-105)}$$

where

S = depth average suspended sediment concentration.

The denominator of Equation IV-105 can be integrated numerically by one of many available solution techniques (e.g. see Carnahan *et al.*, 1969). For the case when a = 0.05 the relationship between Sa and S is given below:

$$\begin{aligned} z &= 0 \longrightarrow Sa = S \\ z &= 0.2 \longrightarrow Sa = 1.8\ S \\ z &= 0.6 \longrightarrow Sa = 4.4\ S \\ z &= 1.0 \longrightarrow Sa = 8.2\ S \\ z &= 2.0 \longrightarrow Sa = 17\ S \\ z &= 5.0 \longrightarrow Sa = 20\ S \end{aligned} \qquad \text{(IV-106)}$$

Based on a knowledge of S, Sa can be estimated from Equation IV-106, and in turn can be used in Figures IV-48 and IV-49.

Typically there is a segregation of particle sizes found in suspension compared with these found in the bed load, and in the immobile bed materials. Based on these differences, the following can be hypothesized:

$$X_s > X_{bl} > X_{im}$$

where

X_s = sorbed pollutant concentration on suspended materials, mass pollutant/mass sediment

X_{bl} = sorbed pollutant concentration on bed load, mass pollutant/mass sediment

X_{im} = sorbed pollutant concentration on immovable sediment, mass pollutant/mass sediment.

Investigations carried out by Miles (1976) appear to support this relationship. Miles collected insecticide residues on stream sediments and in the water column. Results of the DDT analysis of Big Creek, Norfolk County, Ontario, 1973 (DDT was banned in 1970) are as follows:

	Concentration of DDT on Sediments (mass of pollutants/mass of sediments
suspended sediments	110 ppb = X_s
bed load	76 ppb = X_{bl}
immovable bed	26 ppb = X_{im}

Miles (1976) also found that DDT transported in the dissolved phase ranged from 10 to 92 percent of the total transported in the water column. This finding is consistent with the results in Table II-14 which shows that the percent of pollutant transported in the dissolved phase can be high even for pollutants such as DDT as long as the suspended solids concentration is not extremely high.

Contaminant data collected in bedded sediments can be very illuminating. Although in a screening approach it is not anticipated the user will go to the field to collect sediment core samples, some data might be available. Depending on the quantity of data available the following types of information might be determinable:

- The spatial extent of contaminated sediments, and pollutant concentrations in the sediments
- The depth of contaminated sediment
- The quantity of toxicant contained in the sediment
- A time history of pollution levels to determine whether they are increasing or decreasing
- The probable sources of the pollutant, based on the location and quantity of contaminated sediments.

Although extensive sampling is required to accurately determine all of the above items, such programs have been successfully accomplished. For example, an extensive sediment sampling program was conducted in the Hudson River in New York to determine the sources of PCBs in the contaminated sediments, and the degree of contamination (Turk, 1979).

4.9.3 Transport and Transformation Expressions for Toxicants in Rivers

The tools presented in this section can be used to predict instream concentrations of toxicants for a variety of different situations. Specifically, the following scenarios are addressed:

- mixing zone analysis,
- continuous point source discharges,

- continuous nonpoint source discharges,

- desorption from bedded sediments,

- spills and instantaneous release of soluble chemicals, and

- spills of high density chemicals which sink to the river bed.

In contrast to many conventional organic pollutants which degrade into innocuous substances, many toxicants are transformed to other chemicals which can be as harmful or more harmful than the original. Consequently, when toxicants are continuously discharged into a river, in addition to predicting the concentration profile, it is useful to also determine:

- the pollutant's advection rate past a specified location,

- the pollutant's volatilization rate over a specified reach, and

- the pollutant's rate of transformation to other species over a specified reach.

The toxicant's fate is thus segregated into the processes of advection, volatilization, and transformation.

In the following three sections on mixing zones, point sources, and nonpoint sources, the user will find there are different methods of approaching the problems. One way to simplify the analysis is to first assume toxicants act conservatively. The user can then perform a first level analysis to find out whether criteria are violated. If they are not, then a detailed analysis is really not required if the objective is to determine criteria compliance. If violations are predicted, a more detailed analysis of these "hot spots" can be performed by considering the various processes affecting the toxicant in the river. This approach requires more work, but by judiciously applying the tools available, the analyses can be expedited.

4.9.3.1 Mixing Zone Expressions

Section IV-4.1.9 presented earlier delineated one- and two-dimensional mixing zone expressions for conventional pollutants. The one-dimensional expressions need to be extended in order to differentiate between solute and sorbate. To do this, the following expressions for pollutant concentration and the suspended solids concentrations are needed:

$$S = \frac{S_u Q_u + S_w Q_w}{Q_u + Q_w} \qquad \text{(IV-107)}$$

$$C_{to} = \frac{C_{ut} Q_u + C_{wt} Q_w}{D_u + Q_w} \qquad \text{(IV-108)}$$

where

S_u, C_{ut} = concentration of suspended solids and concentration of sum of solute and sorbate in the river above the location of mixing, respectively

S_w, C_{wt} = concentration of suspended solids and concentration of sum of solute and sorbate in the wastewater, respectively.

S, C_{to} = concentration of suspended solids and concentration of sum of solute and sorbate in the river following mixing, respectively.

The dissolved phase concentration, C, of the pollutant at the completion of mixing is given by:

$$C = \frac{C_{to}}{1 + k_p S} \qquad \text{(IV-109)}$$

where

C_{to} and S are found from the two previous expressions.

The concentration of the solute following mixing depends on characteristics of the waste source, the river's flow rate, and the suspended solids concentration in the river and waste source. The solute concentration might also change after mixing with a tributary of very high suspended solids concentration (high S_w), even if it contains no additional pollutant ($C_{wt} = 0$).

Equation IV-108 is particularly useful because it predicts the total instream concentration of toxicant following initial mixing. This is often the critical test in establishing whether or not water quality standards are violated by a point source.

In cases where initial mixing is incomplete (that is the waste is initially diluted with a fraction of the total river flow), the two-dimensional mixing equation shown earlier as Equation IV-4 will more accurately predict C_{to}. Then Equation IV-109 can be used to find the solute concentration.

When there are numerous discharges of the same toxicant, analysis becomes more complicated. The most straightforward method of handling this situation is to sequentially apply Equation IV-108 to the series of discharges to find the concentration as a function of distance downstream. If the solute concentration is needed, then sequential application of Equations IV-108 and IV-109 is required.

The analysis of multiple point sources can be simplified in one of two ways. One, the sources can be transformed to an equivalent nonpoint source by assuming that the toxicant input is uniformly distributed between the series of point sources. This approach is discussed in Section 4.9.3.3. Two, a series of closely grouped point sources can be handled as an equivalent point source. The equivalent point source has a flow rate equal to the sum of the flow rates from the individual plants, or:

$$Q_w = \sum_{i=1}^{n} Q_{wi} \qquad \text{(IV-110)}$$

where

Q_{wi} = flow rate from ith treatment plant
n = number of treatment plants being grouped

The total pollutant load can be expressed in one of two ways. If the concentrations in the wastewater are known then the total loading is:

$$C_w\, Q_w = \sum_{i=1}^{n} C_{wi}\, Q_{wi} \qquad \text{(IV-111)}$$

where

C_{wi} = concentration of toxicant in effluent of ith plant

If the mass emission rates are known instead then:

$$C_w\, Q_w = \frac{\sum_{i=1}^{n} M_i}{5.38} \qquad \text{(IV-112)}$$

where

M_i = mass emission rate of toxicant from ith plant is lbs/day.

The conversion factor 5.38 converts mass emission rate in lbs/day to flow units in cfs and concentration units in mg/l (ppm).

The grouping procedure described above has been applied by the U.S. Environmental Protection Agency (1981) to a case study in Indiana to evaluate the economic impact of toxicant standards. Numbers of point sources were grouped together using a procedure called cluster analysis. The cluster analysis added the loadings of major and minor industrial dischargers within a ten-mile radius of each other. Ten clusters were identified and few violations occurred within them once the best available technology was attained.

For certain applications the object of using a mixing zone equation is to directly find the maximum allowable concentration in the discharge so that the receiving water criteria are not violated. Under these circumstances Equation IV-108 can be rewritten as:

$$(C_{wt})_{max} = \frac{C_{tc}\,(Q_{uc} + Q_w) - C_{ut}\,Q_{uc}}{Q_w} \qquad \text{(IV-113a)}$$

$$= C_{TC}\,\frac{(Q_{uc} + Q_w)}{Q_w}, \text{ when } C_{ut} = 0 \qquad \text{(IV-113b)}$$

where

$(C_{wt})_{max}$ = maximum allowable concentration of the toxicant in the waste discharge so that the water quality criterion is met under critical conditions.

C_{tc} = water quality criterion for the toxicant

Q_{uc} = critical river flow rate (e.g. ${}_7Q_{10}$)

Equation IV-113b is applicable when the concentration of the toxicant is zero upstream of the discharge point.

4.9.3.2 Point Source Discharges

For point sources of toxicants, the pollutant interactions depicted in Figure IV-50 are simulated. While transformation of toxicants is generally more complex than this, in many instances these interactions are sufficient to analyze the instream processes affecting not only point source discharges but also nonpoint source discharges, and instantaneous releases of soluble pollutants. Figure IV-50 reveals that:

- The solute only is assumed to volatilize.

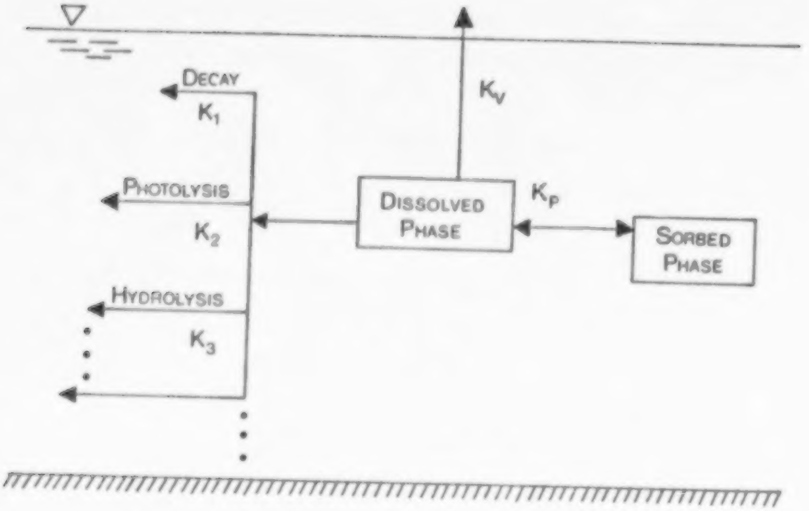

Decay
K_1
Photolysis
K_2
Hydrolysis
K_3
K_v
Dissolved Phase
K_p
Sorbed Phase

FIGURE IV-50 INSTREAM TRANSFORMATION PROCESSES ANALYZED FOR TOXICANTS.

- First order transformation processes degrade only the solute.

- Adsorption and desorption are assumed to occur at rates much faster than other processes.

- No interactions with the bottom sediments occur (this is analyzed in later sections).

Based on these interactions, the concentration profile below a point source of toxicant is expressible as:

$$C = \left\{ C_o - \frac{k'_v}{k'_v + k_i} \frac{P}{K_H} \right\} \exp \left\{ - \frac{k'_v + \sum k_i}{U\,(1 + K_p S)} x \right\} + \left(\frac{k'_v}{k'_v + k_i} \right) \frac{P}{K_H} \qquad \text{(IV-114)}$$

where

C = concentration of dissolved phase of the toxicant at a distance x below the point source

C_o = concentration of the dissolved phase of the toxicant at x = 0 (after the point source discharge has mixed with the river water)

$k_v' = k_v/D$

D = water depth

k_i = individual first order decay rates which are transforming the toxicant (other than volatilization)

P = partial pressure of the toxicant in the atmosphere above the river,

and the remaining variables have previously been defined. Typically the partial pressure is zero, so that Equation IV-114 simplifies to:

$$C = C_o \exp\left[\frac{-\left(k_v' + \sum k_i\right)}{1 + K_pS} \cdot \frac{x}{U}\right] \qquad \text{(IV-115)}$$

The initial dissolved phase concentration is given by:

$$C_o = \frac{C_{to}}{1 + K_pS} \qquad \text{(IV-116)}$$

where

C_{to} was defined by Equation IV-108

The total pollutant concentration, C_t, at any location is:

$$C_t = C\,(1 + K_pS)\ , \qquad \text{(IV-117)}$$

The sorbed phase concentration expressed as mass per unit volume of water is:

$$C_s = C_t - C\ , \qquad \text{(IV-118)}$$

and the sorbed phase concentration expressed as mass per unit mass of sediment is:

$$X = K_pC \qquad \text{(IV-119)}$$

The most direct application of Equation IV-114 or IV-115, plus Equations IV-117 through IV-119 is to find the instream concentration as a function of distance below the point source. There are, however, other uses of the expressions. Consider Equation IV-115, for example. The ratio C/C_o can be directly calculated as a function of distance. Thus the fractional dissolved phase concentration can be calculated without ever knowing the initial concentration C_o. This approach has the advantage of requiring less data. Similarly, the fractional concentration can be calculated for any specified distance, such as the end of a reach. Or, the distance x can be found so that the fractional concentration is some specified number, which may relate to an acceptable level of toxicant. The length of river subjected to unacceptable levels can then be found.

The user might additionally want to know the distribution of pollutant fluxes in terms of advection ($\dot{M}_a$), volatilization ($\dot{M}_v$), and transformation ($\dot{M}_t$). Expressions for these are presented for the case of $P = 0$. These formulae allow the user to predict the fluxes associated with the point source discharge where volatilization is not altered by a background concentration in the atmosphere. Under these conditions:

$$\dot{M} = \dot{M}_a + \dot{M}_v + \dot{M}_t \tag{IV-120}$$

Equation IV-120 states that the rate of entry of the toxicant into the river ($\dot{M}$) equals the rate of advection of that toxicant past some location x_s, plus the rate of volatilization across the water surface between the discharge location and some other specified location plus the rate of transformation of the toxicant to other substances within the water column between the same two locations. By knowing expressions for each of $\dot{M}_a$, $\dot{M}_v$, and $\dot{M}_t$ the user knows the major processes controlling the toxicant's fate within any reach of river.

The mass flux advected past a location x_s is given by:

$$\dot{M}_a = (Q_u + Q_w)\, C + (Q_u + Q_w)\, C_s \tag{IV-121}$$

where the concentrations C and C_s are evaluated at $x = x_s$. The volatilization mass flux is given by:

$$\dot{M}_v = A_c\, k_v'\, C_o\, \frac{U\,(1 + K_p S)}{k_v' + \sum k_i} \left[1 - \exp\left(- \frac{k_v' + \sum k_i}{U\,(1 + K_p S)}\, x_s \right) \right] \tag{IV-122}$$

where

A_c = cross-sectional area of river

and all other terms have previously been defined. In some cases the user might have an estimate of the average dissolved phase concentration, $\overline{C}$, within the reach under consideration. Under these circumstances the volatilization flux is simply:

$$\dot{M}_v = A_s\, k_v\, \bar{C} \tag{IV-123}$$

where

A_s = surface area of the reach under investigation.

The transformation mass flux is expressible as:

$$\dot{M}_t = A_c \sum k_i\, C_o \frac{U\,(1 + k_p S)}{k_v' + \sum k_i} \left[1\text{-exp} \left(- \frac{k_v' + \sum k_i}{U\,(1 + K_p S)}\; x_s \right) \right] \tag{IV-124}$$

Since the sum of Equations IV-121, IV-122, and IV-124 equals the mass emission rate of the toxicant, Equation IV-120 can be used to double check the fluxes calculated.

4.9.3.3 Nonpoint Source Discharge

This section parallels the previous section on point source discharges by presenting expressions for the steady-state concentration profile, and for mass fluxes. In addition to applying this methodology to a nonpoint source, another and possibly more useful application is to express a series of point sources as an equivalent nonpoint source. The equivalent nonpoint source discharge rate is simply the sum of the discharge rates of the pollutant from all the point sources. This approach is not as accurate as analyzing each point source individually but is much faster depending on the number of point sources. For example, suppose a river segment has ten separate point sources located within 50 miles of each other. The most rigorous analysis would consist of considering each point source individually, where mixing zone and point source equations are applied sequentially ten times each. This obviously is a great deal of work for a hand calculation approach. By considering these point sources as a single equivalent nonpoint source, a single equation application is sufficient to analyze the problem. Example IV-5 shown earlier in the BOD section illustrates this procedure.

The solute concentration in a river resulting from a steady nonpoint source of toxicant is:

$$C = \frac{-k_4}{k_3} + \left(C_o + \frac{k_4}{k_3}\right)\left(\frac{Q_o + mx}{Q_o}\right)^{\frac{-k_3}{k_2}} \qquad \text{(IV-125)}$$

where

$$k_2 = \frac{1 + K_pS}{A_c}\ m$$

$$k_3 = k_2 + k_v' + \sum k_i$$

$$k_4 = \frac{C_{tn}}{A_c}\ m - \frac{P}{H}\ k_v$$

C_{tn} = total concentration of toxicant in nonpoint source

$$m = \frac{Q_f - Q_o}{x_1}$$

Q_f = river flow rate at end of nonpoint source
Q_o = river flow rate at beginning of nonpoint source
x_1 = length of nonpoint source.

Equations IV-117 through IV-119 can be used to find C_t, C_s, and X, respectively.

In a manner similar to point source discharges, Equation IV-120 which expresses the mass balance between toxicant inflow rate to the river and loss rate by advection, volatilization, and transformation, is valid. The appropriate expressions are (when P = 0):

$$\dot{M}_a = \underbrace{(Q_o+mx)C}_{\substack{\text{solute}\\ \text{transport}}} + \underbrace{(Q_o+mx)\ Ck_pS}_{\substack{\text{sorbate}\\ \text{transport}}}\ \text{, at} = x_s \qquad \text{(IV-126)}$$

for the advective flux. For the volatilization flux:

$$\dot{M}_v = -k_v' A_c \frac{k_4}{k_3} x_s + k_v' A_s \left(C_o + \frac{k_4}{k_3}\right) \frac{Q_o}{m} \frac{k_2}{k_2-k_3} \left\{\left(\frac{Q_o+mx_s}{Q_o}\right)^{\frac{-k_3}{k_2}+1}\right\} \qquad \text{(IV-127)}$$

For the transformation flux:

$$\dot{M}_t = -\Sigma k_i A_c \frac{k_4}{k_3} x_s + \Sigma k_i A_c \left(C_o + \frac{k_4}{k_3}\right) \frac{Q_o}{m} \frac{k_4}{k_2-k_3} \left\{\left(\frac{Q_o+mx_s}{Q_o}\right)^{\frac{-k_3}{k_2}+1} -1\right\} \qquad \text{(IV-128)}$$

As a first cut analysis, the user might want to assume that the toxicants act conservatively. If criteria are not violated under these circumstances, then criteria will not be violated if decay or transformation processes are included.

4.9.3.4 Desorption of Toxicant from a River Bed

Because many toxicants are transported as sorbate rather than as solute, a significant fraction of the pollutant which enters a riverine system can ultimately be deposited in the bedded sediments. If the toxicant is resistant to degradation processes it can remain in the sediments for extended periods of time. During this time, the toxicant can slowly be desorbed back into the water column or scoured into suspension.

Figure IV-46 shown earlier illustrated an idealization of the process of desorption of a toxicant from bedded sediments. The process can be described as follows. Supposed the average concentration of the pollutant in the bedded sediment is X_o when the analysis begins (called t = 0). The concentration X, at any later time is estimated from mass balance considerations as:

$$X = \begin{cases} X_o \text{ , for } x > \dfrac{U\delta t}{M_s K_p} \\ 0 \text{ , otherwise} \end{cases} \qquad \text{(IV-129)}$$

where

X_o = concentration of pollutant in bed at some time t = 0
M_s = mass of contaminated sediment per unit area of river bed, g/cm^2
U = stream velocity, cm/sec
δ = equivalent depth of water in sediment M_s, cm
K_p = partition coefficient

Equation IV-129 reveals that desorption can be interpreted as a frontal phenomenon where desorption is completed at one location before progressing downstream. Based on this interpretation, an effective removal velocity of the front is:

$$U_e = \frac{U\,\delta}{M_s K_p} \qquad \text{(IV-130)}$$

The time T_d required to desorb the toxicant over any specified distance is:

$$T_d = x_L/U_e \qquad \text{(IV-131)}$$

where

x_L = length of contaminated river segment

During the period of desorption the average concentration in the water column is:

$$C = \begin{cases} \dfrac{X_o \delta}{K_p D} \text{ for } x > U_e t & \text{(IV-132)} \\ 0 \quad \text{, otherwise} & \text{(IV-133)} \end{cases}$$

To use Equations IV-129 through IV-133, estimates for X_o, M_s, and δ are required. If both the mass of contaminated sediment per unit area of river bed (M_s) and the mass of toxicant in the sediments are known, then X_o can be determined. Conversely, if both X_o and the total mass of toxicant in the sediments are known, then M_s can be calculated.

In lieu of having data on M_o and δ, these quantities can be estimated based on the depth of contaminated sediments by using Table IV-39. In addition to the depth, the percent solids by weight must be estimated. This parameter generally increases with depths and can be chosen as 50 percent, unless better data are available. The data in Table IV-39 were derived from the following two equations:

$$M_s = \frac{D_c}{10\left(1/S_s + \frac{100-P}{P}\right)} \qquad \text{(IV-134)}$$

and

$$\delta = \frac{S_s \times D_c \left(\frac{100-P}{P}\right)}{1 + S_s\left(\frac{100-P}{P}\right)} \qquad \text{(IV-135)}$$

where

M_s = mass of contaminated sediment, g/m^2
δ = equivalent water depth, mm
S_s = specific gravity of solids
D_c = depth of contamination, mm

In cases where the depth of contamination exceeds 100 mm the equations can be used in lieu of Table IV-39.

The Hudson River in New York State provides an illustration of an extreme case of PCB contamination (Turk, 1980). Between 1951 and 1977 PCBs were discharged from point sources near Fort Edward and Hudson Falls, about 80 km (50 mi) above Albany, New York. Figure IV-51 shows the general vicinity.

During this time period the mass emission rate of PCBs decreased from 15 kg/day (33 lbs/day) to less than 1 g/day (0.002 lbs/day). PCB concentration in the bottom materials range from about 200 μg/g near Fort Edward to about 4 μg/g near Waterford, about 70 km (43 mi) downstream. In 1975 the New York State Department of Environmental Conservation began a study to determine the source of contamination. At that time they estimated that the total mass of PCBs in the bottom sediments was 225,000 kg (500,000 lbs).

TABLE IV-39

MASS OF CONTAMINATED SEDIMENTS AND EQUIVALENT WATER DEPTH AS A FUNCTION OF DEPTH OF CONTAMINATION

Depth (mm)	Percent Solids by Weight	M_s (g/cm^2)	δ(mm)
1	20	0.02	0.9
	50	0.06	0.6
	80	0.11	0.3
5	20	0.11	4.5
	50	0.30	3.0
	80	0.55	1.4
10	20	0.23	9.1
	50	0.60	6.0
	80	1.1	2.7
20	20	0.45	18.
	50	1.2	12.
	80	2.2	5.5
50	20	1.1	45.
	50	3.0	30.
	80	5.5	14.
100	20	2.3	91.
	50	6.0	60.
	80	11.0	27.

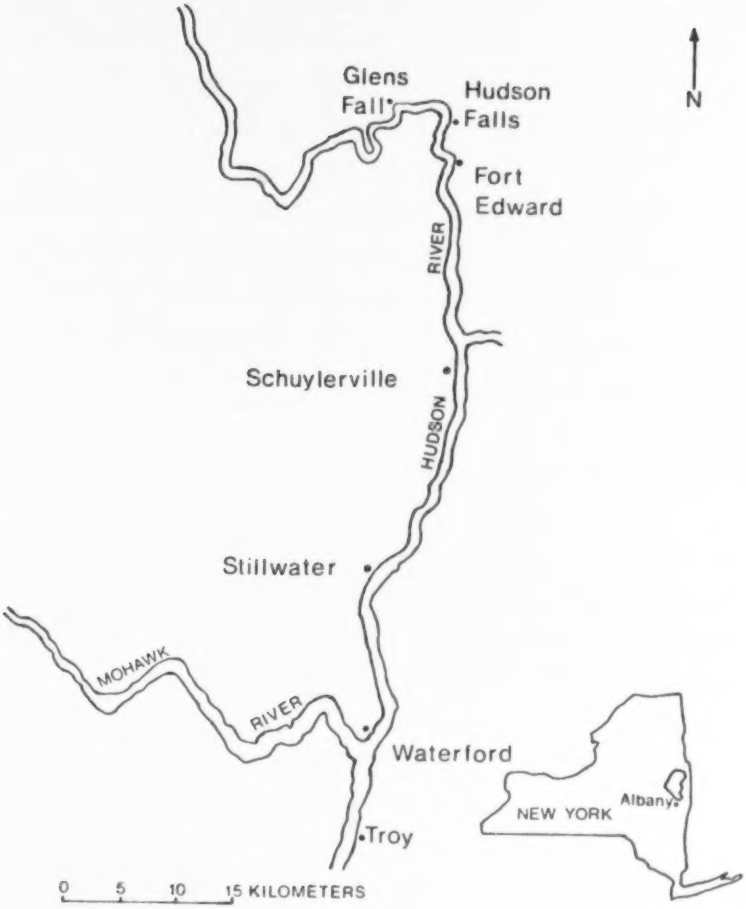

Glens Fall
Hudson Falls
N
Fort Edward
RIVER
HUDSON
Schuylerville
Stillwater
MOHAWK
RIVER
Waterford
Troy
NEW YORK
Albany
0 5 10 15 KILOMETERS

FIGURE IV-51 LOCATION MAP OF HUDSON RIVER, NEW YORK.

It has been found that PCBs are being naturally desorbed from the river bed under moderate and low flow conditions. The estimated transport rates are:

- at Glen Falls = 0.0 kg/day (above discharge)
- at Schuylersville = 4.0 kg/day
- at Stillwater = 5.0 kg/day
- at Waterford = 4.0 kg/day (70 km downstream)

It is interesting to note that these transport rates are approximately 30 percent as high as the original point source mass emission rates. At a desorption rate of about 4 kg/day, the river between Glen Falls and Waterford would be rid of PCBs in about 150 years.

Turk (1980) found that flood events transport large quantities of PCBs, although this transport mechanism is only operative periodically. Turk estimated that due to the combined removal rates of PCBs during high flow periods (by scour) and during low flow periods (by desorption), the residence time of PCBs above Waterford would be about one century.

EXAMPLE IV-18

For discharges of 600 m^3/sec or less, it has been found that the Hudson River bed provides 4 kg/day of PCBs to the water column at locations between Schuylersville and Waterford, New York. Determine the PCB concentration in the water column at the following two flow rates:

a. 600 m^3/sec
b. 50 m^3/sec.

Compare these concentrations to the freshwater criterion of 0.001 μg/l promulgated in the "Red Book".

Since the mass emission rate and river flow rate are known, Equation IV-11 can be rearranged to yield the total instream concentration:

$$C_t = \frac{M}{86.4Q}$$

where

M = mass loading, kg/day
C_t = concentration of pollutant, ppm
Q = flow rate, m^3/sec

For the problem at hand,

M = 4 kg/day
Q = 50 and 600 m^3/sec

For $Q = 600\ m^3$/sec,

$$C_T = \frac{4}{86.4 \times 600} = 0.08 \times 10^{-3} \text{ ppm}$$

$= 0.08\ \mu g/l$, or 80 times the Red Book criterion

For $Q = 50\ m^3$/sec,

$$C_T = \frac{4}{86.4 \times 50} = 0.9 \times 10^{-3} \text{ ppm}$$

$= 0.9\ \mu g/l$, or 900 times the criterion

As a second part to the problem estimate the time required to remove the PCBs in the sediment by desorption (ignoring scour), assuming the desorption rate of 4 kg/day is not known. Base the calculations on Table IV-39 or Equations IV-130 and IV-131. Use the following data:

- depth of contaminated sediment = 600 mm
- river velocity = 1 fps
- partition coefficient : 10^3 to 10^4

Because the depth of contamination exceeds the maximum value tabulated in Table IV-39, Equations IV-134 and IV-135 are used instead. Assuming $S_s = 1.5$ and $P = 80$,

$$M_s = \frac{600}{10\left(\frac{1}{1.5} + \frac{100-80}{80}\right)} = 65 \text{ g/cm}^2$$

$$\delta = \frac{1.5 \times 600 \left(\frac{100-80}{80}\right)}{1 + 1.5\left(\frac{100-80}{80}\right)} = 160 \text{ mm} = 16 \text{ cm}$$

The effective transport velocity is:

$$U_e = \frac{U \times 16}{65 \times 10^4} = .25 \times 10^{-4}\ U \quad \text{for } K_p = 10^4$$

and

$$U_e = \frac{U \times 15}{65 \times 10^3} = .25 \times 10^{-3}\ U \quad \text{for } K_p = 10^3$$

The time required for desorption over the 70 km (43 mi) reach is:

$$T = \frac{43 \times 5280}{.25 \times 10^{-4} \times 1} \text{ Sec} = 290 \text{ year for } K_p = 10^4$$

and

$$T = 29 \text{ years for } K_p = 10^3$$

Probably the biggest unknown in this problem is K_p. Based on a range of K_p from 10^3 to 10^4, the time of desorption ranges from 29 to 290 years, within the range predicted from observed desorption rates.

END OF EXAMPLE IV-18

4.9.3.5 Instantaneous Releases of Low Density Toxicants

Many toxicants have specific gravities less than or equal to unity. Should a toxicant less dense than water be spilled in its pure form, the toxicant can ride atop the water body for a period of time, while (perhaps) being rapidly volatilized and photolyzed as it becomes entrained and dissolved in the river.

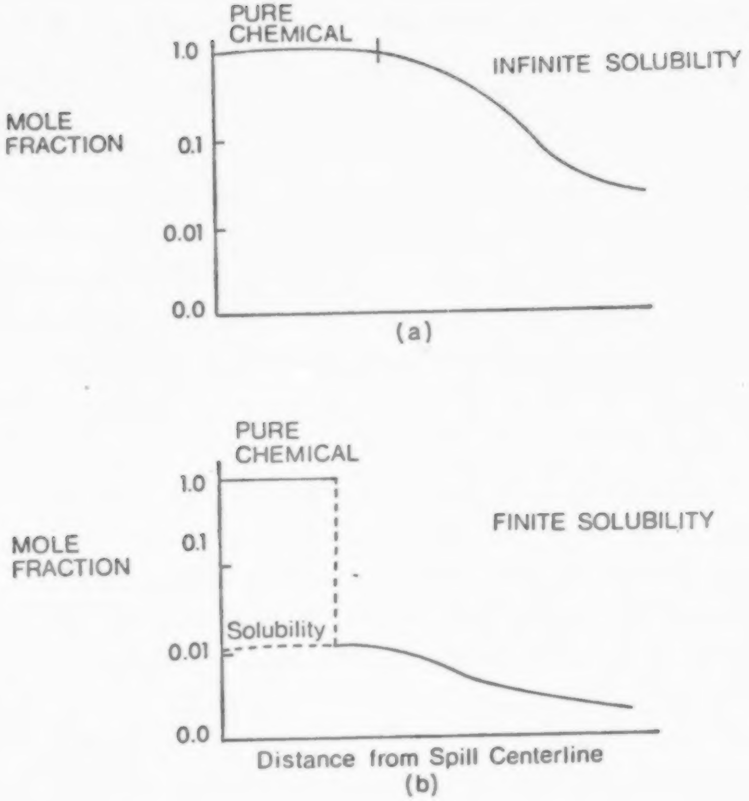
Analysis of releases of low density pollutants is complicated and, in many cases, beyond the scope of hand calculation analyses. Often spills of toxicants occur over a part of the river, so the resultant movement is three-dimensional because the toxicant spreads laterally, longitudinally, and vertically due to turbulence and advection. Buoyant spreading and mixing can further complicate the dispersal process.

Toxicant spills can occur in numerous ways. In one instance the toxicant may be discharged directly onto the surface of the river, and depending on the rate of mixing with ambient water a significant portion could volatilize directly from the pure phase. On the other hand submerged spills may result in the chemical becoming mixed with river water before it reaches the water's surface. Under these circumstances volatilization fluxes will not be as great.

When a chemical is spilled in pure form, the time required for the chemical to mix with the river water depends, in addition to other factors, on the solubility of the chemical. Some chemicals may be highly soluble in water (essentially infinitely soluble) while others may have a very low solubility. Figure IV-52 illustrates these two different situations.

Figure IV-52a shows the case of a toxicant of infinite solubility. The toxicant maintains its pure state (mole fraction equals unity) for some distance away from the spill site, and then the mole fraction gradually begins to decrease as the chemical mixes with water. Figure IV-52b illustrates the same basic situation, except that the toxicant has a finite solubility. In this case there will be a rapid drop between the mole fraction of the pure toxicant (unity) and the mole fraction at solubility (much less than unity). For the pure phase toxicant shown in Figure IV-52b to become mixed in water at concentrations at or below the solubility limit might require a substantial amount of water.

Based on the discussions in the previous paragraphs, tools for analyses of the following will be presented:



(a)

(b)

FIGURE IV-52 HYPOTHETICAL CONCENTRATION DISTRIBUTIONS OF FINITELY SOLUBLE AND INFINITELY SOLUBLE TOXICANTS.

- Volatilization mass flux from a pure toxicant contained within a fixed area.

- The fate of a highly soluble toxicant which mixes instantaneously with the river water.

- The fate of a low solubility toxicant which mixes with a finite volume of river water.

Toxicants which exist in the gas phase under atmospheric pressure and typical natural temperatures are excluded from analysis here, even though they might be transported as a liquid under high pressure (e.g. liquified chlorine). If a tank transporting such a chemical were to rupture under water, the chemical would boil and most of the gas would rapidly escape into the atmosphere. Some of the gas would however become dissolved in the river water during ascent of the bubbles.

4.9.3.5.1 Volatilization of Toxicant in Pure State

This section will present a method to predict the volatilization mass flux rate of a pure chemical, and the time required to volatilize a known amount of the chemical which occupies a specific area of river surface. The volatilization flux rate is given by:

$$F = \frac{k_g \cdot P_v \cdot MW}{R_u T} = \frac{k_g \cdot P_v \cdot MW}{82.06\ T} \qquad \text{(IV-136)}$$

where

F = volatilization mass flux, $g/cm^2/hr$
P_v = saturation vapor pressure of pure liquid toxicant, atm
MW = molecular weight of toxicant
T = temperature of ambient water, ^oK
k_g = gas phase transfer coefficient, cm/hr.

The expression for the gas phase transfer coefficient was shown earlier in Equation II-46. A suggested default value is 3000 cm/hr. The saturation vapor pressure of a number of toxicants were shown earlier in Tables II-5 through II-9. Weast (1969) also contains extensive data.

Based on the amount of pure toxicant (M) contained within a spill area (A), the time required to volatilize the chemical is:

$$t = \frac{M}{10 \times F \times A} \quad \text{(IV-137)}$$

where

t = time, hr
M = mass, kilograms
A = area, m^2

This expression is limited to situations where the spill area A is of constant size over the period of volatilization so it is not applicable to unconfined spills where the area could change rapidly with time.

4.9.3.5.2 Analysis of Chemicals Which Instantaneously Mix

Depending on the mass of spilled toxicant and its solubility, the spilled toxicant may rapidly attain concentrations in the water column below solubility. Under these circumstance, Equation IV-138 presented below can be used. The analysis below assumes that Henry's Law is valid (e.g. the mole fraction of dissolved chemical is much less than 1.0) which is reasonable for many toxicants only moments after a spill.

It is worthwhile to calculate the volume of water required for a mass M of spilled chemical to be diluted to its solubility limit. This can provide a rough idea as to whether mixing is likely to be "instantaneous" or not. Suppose that a mass M of spilled chemical has a solubility C_s. The volume of water needed to be mixed with the pure chemical so that the solubility limit is achieved is:

$$V_o = \frac{M \times 10^6}{C_s} \tag{IV-138}$$

where

M = mass of spill, kg
C_s = solubility, mg/l
V_o = volume of water, m^3

The concentration profile resulting from an instantaneous spill (and assuming concentrations at or below the solubility limit are rapidly attained) is expressed by:

$$C = \frac{M_D}{2A_c \sqrt{\pi D t}} \exp \left[\frac{-(x-ut)^2}{4Dt} - k_e t\right] + \frac{k_v'}{k_v' + \Sigma k_i} \cdot \frac{P}{K_H} \left[1 - \exp(-k_e t)\right] \tag{IV-139}$$

where

C = dissolved phase concentration

$k_e = \frac{k_v' + \sum k_i}{1 + K_p S}$

$M_D = \frac{M}{1 + K_p S}$

M = total mass released

and the remaining variables have been previously defined. In most instances the user would like to predict the maximum concentrations remaining in the river for different elapsed times following the spill, given by the peaks in Figure IV-53. Under such conditions, and assuming P = 0, Equation IV-139 simplifies to:

$$C_{max} = \frac{M_D}{2A_c \sqrt{\pi D t}} \exp(-k_e t) \tag{IV-140}$$

The various components of the mass balance at time t follow (for P = 0).

Mass of dissolved pollutants $M_D(t = t_s)$:

$$M_D(t = t_s) = M_D \exp(-k_e t_s) \tag{IV-141}$$

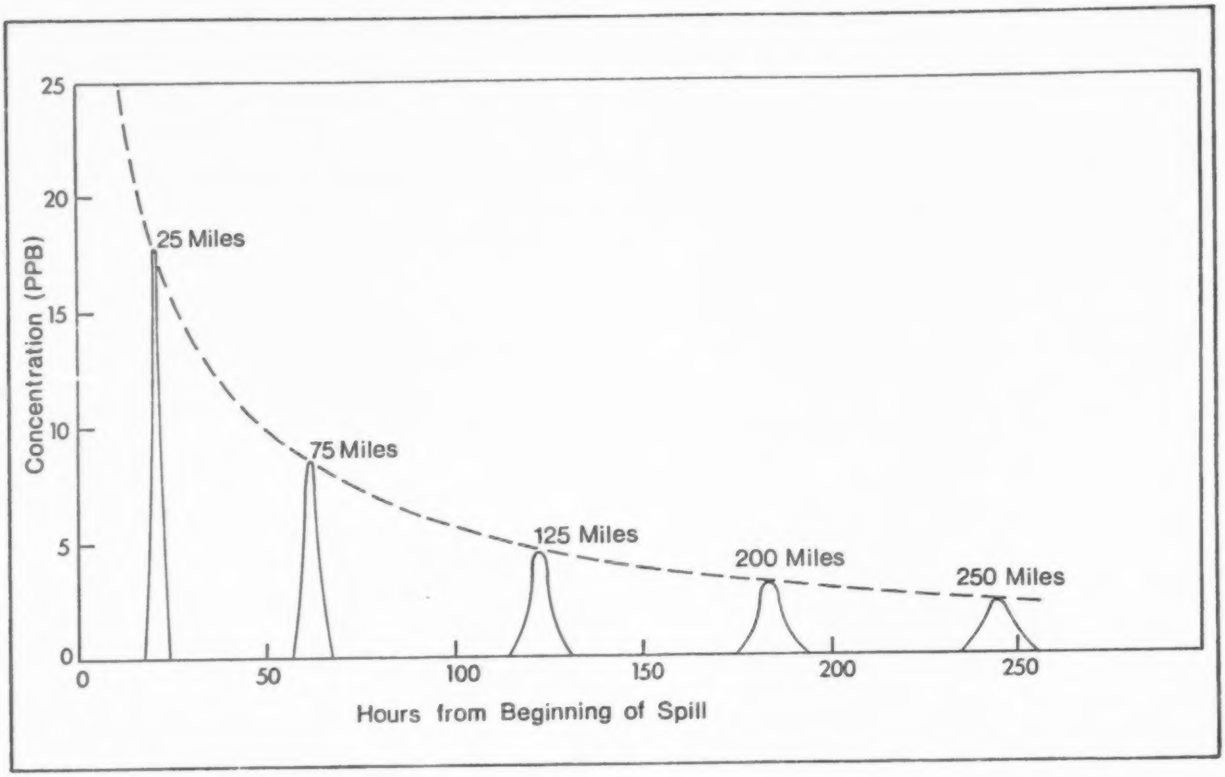


FIGURE IV-53 HYPOTHETICAL DISTRIBUTION OF TOXICANT AT VARIOUS LOCATIONS FOLLOWING A SPILL

Mass of sorbed pollutants $M_S(t = t_s)$:

$$M_s = K_p S \, M_D \exp(-k_e t_s) \qquad \text{(IV-142)}$$

Mass of pollutant which has volatilized $M_v\ (t = t_s)$:

$$M_v\ (t = t_s) = \frac{M_D\ k'_v}{k_e} \left[1-\exp(-k_e t_s)\right] \qquad \text{(IV-143)}$$

Mass of pollutant which has decayed $M_{Dk}\ (t = t_s)$:

$$M_{Dk}\ (t = t_s) = \frac{M_D \Sigma k_i}{k_e} \left[1 - \exp(-k_e t_s)\right] \qquad \text{(IV-144)}$$

Equations IV-140 through IV-144 allow the user to assess the fate of the pollutant for any desired time t_s following the spill.

A direct extension of the instantaneous pollutant release in a plane is the volumetric release, where the pollutant is effectively released within some initial volume of water. For this case, the dissolved phase concentration is:

$$C = \frac{M_D}{2V_o} \quad \text{erf} \left[\left(\frac{X - Ut}{\sqrt{4Dt}}\right) - \text{erf} \left(\frac{X-L-Ut}{\sqrt{4Dt}}\right)\right] \quad \left(\exp(-k_e t)\right) \qquad \text{(IV-145)}$$

where

L = length of zone of initial contamination

erf = the error function.

and all other variables have been previously defined. The location of the maximum concentration for any time t_s after release is approximately given by:

$$x = Ut_s + L/2 \qquad \text{(IV-146)}$$

4.9.3.6 Spill Analysis of High Density Toxicants

Spills of hazardous chemicals have been of concern for quite a number of years, and interest will increase as the quantity and variety of toxicants transported increase. In past years the primary emphasis has been on analysis and containment of oil spills. This has probably been for a number of reasons:

- Large quantities of oil are transported, and are therefore subject to more frequent spills.

- The environmental consequences of an oil spill can be severe and visually offensive.

- Oil floats, so oil spills are easy to detect and monitor.

In contrast to oil, many hazardous chemicals have specific gravities greater than one, so that in their pure form, they tend to sink in water. Table IV-40 lists some such chemicals. Chlorine, although it may be transported under pressure as a liquid, is a gas under atmospheric conditions. Even so, if a liquid chlorine barge were involved in an accident on a river some of the chlorine could become dissolved in the water since the solubility of chlorine in water is 50,000 mg/l, although most would probably gasify and form a toxic cloud.

The chemicals shown in Table IV-40 are generally either slightly soluble (10 to 10,000 ppm) or soluble (10,000 to 1,000,000 ppm). In any case the solubility levels generally exceed or greatly exceed proposed water quality criteria. Thus if a mass of chemical were spilled into a river, it is to be expected that concentrations near the chemical's solubility limit could be detected in the immediate vicinity of the spill. As the chemical is dissolved and travels downstream, it could eventually become mixed over the channel cross-section and expose all organisms living within the water column (and perhaps those living in the bedded sediments as well) to its effects. With increasing distance the concentrations of the toxicant will decrease to reflect the additional mixing afforded by the flow of the entire river, plus dispersion, degradation, and volatilization processes.

TABLE IV-40
WATER-SOLUBLE, HIGH DENSITY ($\rho>1$), IMMISCIBLE CHEMICALS

Species	Density in air (g/cm^3)	Solubility in water (mg/l)	Interfacial Tension (dynes/cm)[a] Air	Water	Vapor
Acetic acid	1.06	50,000	68.0_{30°	-	27.8_{20°
Acetic anhydride	1.087	500,000	-	-	32.7_{20°
Acetophenone	1.03	5,550	-	-	39.8_{20°
Aniline	1.022	34,000	44.0	-	42.9_{20°
Benzaldehyde	1.04	1,000	40.04	15.51_{20°	-
Benzyl alcohol	1.043	46,000	39.0_{20°	$4.75_{22.5^\circ}$	39.0_{20°
Bromine	2.93	41.700	41.5_{20°	-	41.5_{20°
Carbon disulfide	1.26	2,200	-	48.36_{20°	-
Carbon tetrachloride	1.595	500	-	45_{20°	26.95_{20°
Chlorine (liquid)[b]	3.2	50,000	-	-	18.4_{20°
Chloroform	1.5	5,000	27.14_{20°	32.8_{20°	-
Chloropthalene			-	40.74_{20°	-
Dichloroethane	1.256	9,000	23.4_{35°	-	-
Ethyl bromide	1.431	10,600	-	31.2_{20°	24.15_{20°
Ethylene bromide	2.18	4,300	-	36.54_{20°	38.37_{20°
Furfural	1.159	83,100	43.5_{20°	-	43.5_{20°
Glycerol	1.26		-	63.4_{18°	-
Hydrogen peroxide	1.46	50,000	-	-	$76.1_{18.2^\circ}$
Mercury[c]	13.54	.0005	470	375_{20°	-
Naphthalene	1.15	30	28.8_{127°	-	28.8_{127°
Nitrobenzene	1.205	1900	43.9_{20°	-	43.9_{20°
Phenol	1.071	67,000	40.9_{20°	-	40.0_{20°
Phenylhydrazine	1.097		-	-	46.1_{20°
Phosphorus trichloride	1.5	50,000	-	-	29.1_{20°
Trichloroethane	1.325	10	22_{144°	-	-
N-Propylbromide	1.353	2,500	-	-	19.65_{20°
Quinoline	1.095	60,000	45.0_{20°	-	-
Tetrachloroethane	1.60	3,000	$36.3_{22.5^\circ}$	-	-
Water[b]	1.00	N.A.	73.05_{18°	N.A.	72

[a] In air, water, and its own vapor. Temperature is °C.

[b] Under pressure.

[c] Mercury and water data included for reference.

From: Thibodeaux (1979)

A technique is presented here to estimate the concentration which can exist in the water column and the duration of the elevated levels following a spill. In particular tools are presented to predict:

- The concentration of toxicant in the water column at the downstream end of the spill.
- The concentration of the toxicant after it has become completely mixed with the entire river.
- The time required to dissolve the spilled toxicant.
- The amount of toxicant remaining sorbed to the bottom sediments and in the pore water following dissolution.

It is, of course, more accurate but more costly to measure concentrations directly rather than predicting them. However, since the toxicant is "somewhere" on the river bottom, and might not be immobile, detecting the location of the toxicant will take time. By estimating the dissolution time of the spill, it can be determined if it is feasible to even set up and carry out a sampling program.

The tools delineated above are useful not only to analyze spills which have occurred, but also for answering hypothetical questions which relate to the consequence of spills based on river traffic, sizes of containers, kinds of toxicants being transported, and characteristics of the rivers. Based on this information the user can evaluate possible "spill scenarios" to predict impacts before they occur. Such information would be useful to formulate post-spill responses. In situations where a spill of a toxicant would produce extreme consequences, provisions could be made to mitigate the consequences before they occur.

4.9.3.6.1 Description of Spill Process

Spills which contaminate rivers can be the result of a variety of accidents: leaking barges, broken pipelines, highway accidents, and clandestine dumping. The scope here is limited to those situations where the toxicant has been deposited on the bottom of the river. This situation is most likely to result from an accident on or under the water's surface. Figure IV-54 conceptualizes what might happen when a barge carrying a high density pollutant ruptures.

Depending on the volume of contaminant, the size of the hole, among other factors, the toxicant might issue from the barge as a continuous jet. However, because the volumetric flow rate of the jet is probably small, and perhaps even intermittent, the toxicant probably breaks up into drops of various sizes as it falls through the water column. Some of the finest drops might never reach the stream bed, but rather be transported in suspension within the water column, and gradually dissolve. The majority of the toxicant may settle on the river bed and form drops, globs, or pools (using the terminology of Thibodeaux, 1979). The drop size depends on the intrafacial tension and density differences between the toxicant and the water (Hu and Kintner, 1955). Pools tend to form in the valleys of sand waves, and occur when large drops or globs coalese. Thibodeaux (1980) provides techniques to estimate the residence time of drops, globs, and pools. For the simplified analyses here the spill is assumed to be in the shape of a continuous pool.

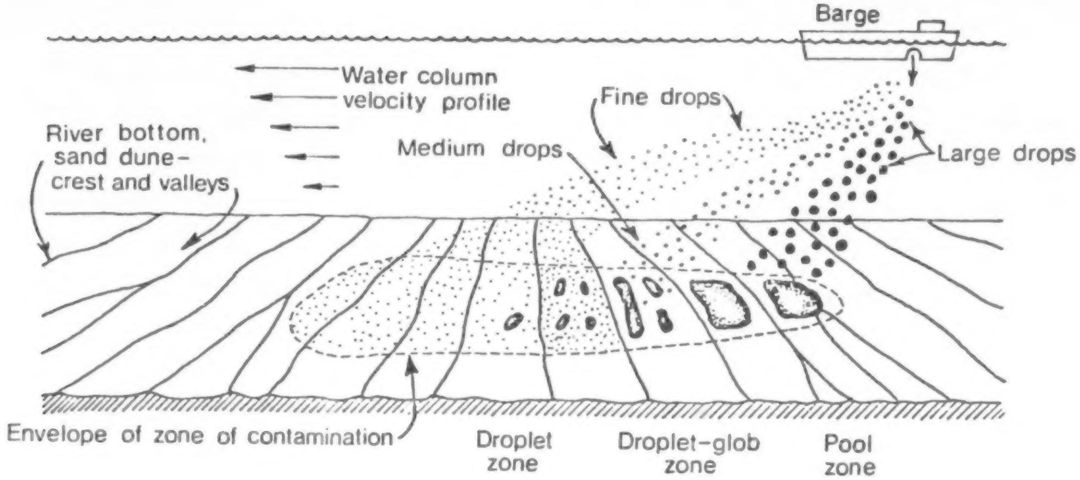

Barge
Water column
velocity profile
Fine drops
River bottom,
sand dune-
crest and valleys
Medium drops
Large drops
Envelope of zone of contamination
Droplet
zone
Droplet-glob
zone
Pool
zone

FIGURE IV-54 ILLUSTRATION OF HYPOTHETICAL SPILL INCIDENT (FROM THIBODEAUX, 1979).

4.9.3.6.2 Fate of Pollutant Following Settling

Once the toxicant has settled on the river bed its fate is governed by numerous processes. Depending on the texture of the bottom materials (e.g. sands, cobbles, boulders), the density of the toxicant, and its interfacial tension, the toxicant could settle in deep depressions, and dissolution would be slowed.

Many pollutants have large partition coefficients so that sorption to bottom sediments is significant. The characteristics of the sediments affect the partition coefficient, but in many cases sorption can compete with dissolution as a major process controlling the pollutant's fate. Although transformation processes other than sorption and dissolution are operative the moment the toxicant enters the water, they are not considered here.

In September 1974 an electrical transformer being loaded onto a barge fell into the Duwamish Waterway in the State of Washington (Thibodeaux, 1980). 260 gallons of Aroclor 1242, a PCB mixture of specific gravity 1.4, were spilled into the river. Divers observed that pools of free PCB on the bottom moved back and forth with the tide. Pools of PCBs were removed from the bottom using suction dredges, and a second stage operation involved a high solids dredge. Probably due to its low solubility (0.2 ppb) and high sorption characteristics, much of the PCB was recovered (from 210 to 240 gallons).

4.9.3.6.3 Predictive Tools

It is hypothesized that a toxicant spill contaminates an area of width W_s and length L_s, where the length is measured in the flow direction. The toxicant which reaches the river bed is assumed to be highly concentrated, and its dissolution is controlled by a thin layer immediately above where molecular diffusion limits the vertical flux of the pollutant. Above this layer the toxicant is rapidly entrained into the river. There are several expressions available to determine the thickness of the diffusion layer (e.g. Novotny, 1969 and Mills, 1976). The expression developed by Mills will be used here, because the required information is easier to attain while the two approaches appear to give comparable results. The expression is:

$$\delta_d = \frac{11.6 \cdot 1.49 \, \nu \, R_h{}^{1/6}}{\sqrt{g} \, Un} \qquad \text{(IV-147)}$$

where

δ_d = thickness of diffusive sublayer
ν = dynamic viscosity of water
R_h = hydraulic radius of the river
U = river velocity
n = Manning's coefficient

Just downstream from the spill zone, but before complete mixing with the river, the concentration of the toxicant in the water column is:

$$C_L = (C_o - C_s)\exp\left(-\frac{D_{cw}L_s}{\delta_d H U}\right) + C_s \qquad \text{(IV-148)}$$

where

C_o = background concentration of chemical
C_s = solubility of chemical in water
D_{cw} = diffusion coefficient of chemical in water
H = water depth
U = river velocity

The concentration at the location of complete mixing is

$$C_{WM} = C_L \frac{W_s}{W} + C_o\left(1 - \frac{W_s}{W}\right) \qquad \text{(IV-149)}$$

where

W_s = spill width
W = river width

The time T_d required to dissolve the chemical is:

$$T_d = \frac{M_D}{C_L U H W_s} \qquad \text{(IV-150)}$$

where

M_D = total amount of pollutant which is dissolved (an amount less than or equal to the amount spilled).

As the spilled toxicant dissolves in the flowing river water, it concurrently diffuses into the immobile bedded sediments, where a portion is sorbed onto the sediments. Consequently, some residual toxicant will remain in the bottom sediments following the initial dissolution phase. The residual will then slowly diffuse and desorb back out into the river, although diffusion deeper into the sediments can also occur because of the concentration gradient. The time required for the residual toxicant to naturally desorb and diffuse back into the water column can greatly exceed the original period of dissolution.

The quantity of toxicant which resides in the sediments following the initial dissolution period can be predicted as follows. It is assumed that the dissolution and downward diffusion/sorption proceed independently until all the spilled toxicant has been removed. The time t can be found such that this statement is true. From a practical standpoint, the user can simply determine the time required for complete dissolution, and then find the total mass which would have diffused/sorbed into the bottom sediments during this period. Since this approach accounts for more toxicant than was originally present, the time period should be decreased by the fractional amount of toxicant created. If the amount of excess toxicant is no more than 15 percent of the total amount spilled, then a time adjustment is not required.

Based on the processes of sorption and diffusion the vertical profile of dissolved chemical in the river bed at time t following the appearance of the toxicant on the bottom is given by:

$$\frac{C - C_b}{C_s - C_b} = 1\text{-erf}\left(\frac{z}{\sqrt{4D_p t}}\right) \qquad \text{(IV-151)}$$

where

C = concentration of dissolved chemical in the pore water, in units of mass of dissolved chemical per unit volume of pore water

C_b = background concentration of chemical in pore water

C_s = solubility of chemical in water

z = vertical distance, measured downward from the sediment-water interface

$$D_p = D_e / \left(1 + \rho_s K_p \frac{1-n}{n}\right)$$

D_e = effective molcular diffusion coefficient
ρ_s = density of sediments
K_p = partition coefficient
n = porosity of porous medium

From Equation IV-151, the total mass of pollutant found in the sediments at time t is:

$$M_T = \int \left(C + C_s\right) n dV \qquad \text{(IV-152a)}$$

$$= A_c n \int \left(C + C_s\right) dZ \qquad \text{(IV-152b)}$$

where

A_c = spill area
C_s = concentration of pollutant sorbed to sediments, per unit volume of pore water

C_s can be related to C by:

$$C_s = C_{\rho_s k_p} \left(\frac{1-n}{n}\right) \qquad \text{(IV-153)}$$

Combining Equations IV-151, IV-152 and IV-153 the total mass in the sediment is:

$$M_T = 0.563_n C_s \left(1 + \rho_s k_p \ \frac{1-n}{n}\right) A_c \sqrt{4 D_p t} \qquad \text{(IV-154)}$$

EXAMPLE IV-19

The following is an excerpt from Chemical Engineering Volume 80, September 3, 1973, as reported in Thibodeaux (1979).

> "Approximately 1.75 x 10^6 lbs of chloroform were released from a barge that sank near Baton Rouge, Louisiana, and the chemical began flowing down the Mississippi River toward the Gulf of Mexico. Although state health officials did not push the panic button, noting that they did not anticipate too much trouble from the accident, the U.S. Coast Guard warned downriver communities to keep a close surveillance on their water supply systems, particularly if intakes were close to the river bottom (chloroform is heavier than water)."

Based on the low flow conditions and the time history of the chloroform concentration much of the chloroform (of specific gravity 1.5) was initially deposited on the river bed. Determine the fate of the chloroform during the first few days following the spill. The following processes are considered:

- dissolution into the main body of the water,
- diffusion and sorption into the bottom sediments,
- volatilization into the atmosphere, and
- sorption to suspended sediments.

Since chloroform is highly volatile and does not have a strong tendency to sorb to solids, volatilization is an important process controlling its fate, while sorption is not. The following analysis substantiates this statement.

The data pertinent to the spill are (Thibodeaux, 1979; Neely *et al.*, 1976):

- river flow rate = 7590 m^3/sec (268,000 cfs)
- width of river = 1220 m = 4000 ft

- river velocity = 56.3 cm/sec = 1.85 ft/sec
- water depth = 11 m = 36.3 ft
- diffusion coefficient of chloroform in water = 1×10^{-5} cm^2/sec
- length of spill zone = 180 m = 590 ft
- background chloroform concentration = 5 ppb

Using a Manning's n of 0.03, the diffusion layer thickness is:

$$\delta = \frac{11.6 \times 1.49 \times .915 \times 10^{-5}}{\sqrt{32.2} \times 1.85 \times 0.03} \times (36)^{1/6} = 9 \times 10^{-4} \text{ ft} = 2.8 \times 10^{-2} \text{ cm}$$

The average concentration of chloroform in the water just below the spill zone during the period of dissolution is:

$$C_L = (5 \times 10^{-3} - 8200) \exp\left(\frac{-1. \times 10^{-5} \times 180}{2.8 \times 10^{-2} \times 11. \times 56.3}\right) + 8200$$

$$= 850 \text{ ppb}$$

In order to estimate the time required to dissolve the chloroform the average width of the spill zone is required. The width is estimated to be 256 ft (78 m) (Thibodeaux, 1981).

Based on these data the dissolution time is:

$$T_d = \frac{0.9 \times 1.75 \times 10^6}{5.38 \times .850 \times 1.85 \times 156 \times 36.3} = 20 \text{ days}$$

The factor 0.9 is used in the above expression because about 10 percent of the spill dissolved before ever reaching the bottom (Neely et al., 1976).

The amount of chloroform which diffused and sorbed into the sediments during this time period (20 days) will be estimated. The porosity of the sandy bottom is approximately 0.35, and the partition coefficient is assumed to be 1.0. This is a realistic value based on K_{ow} = 93 (see Table II-5). The total mass contained in the sediments after 20 days is:

$$M_{Total} = .35\ (180 \times 78)\ \left(1+2.65 \times 1 \times \frac{.65}{.35}\right) 8200 \sqrt{\frac{4.10^{-5} \times 20 \times 86400}{1 \times 2.65 \times 1 \times \frac{.65}{.35}}}$$

$$\times\ 10^{-2-3} \times (5-4.437) \approx 6000 \text{ kg}$$

6000 kg is less than 2 percent of the total mass which reaches the bottom (715,000 kg). Based on this result, it is not likely that the dissolution period is markedly affected by diffusion of the chloroform into the bottom sediments. Because of the vertical concentration gradient that has been established in the sediment profile, some of the chloroform will temporarily continue to diffuse downward after the dissolution period. Hence concentrations in the water column due to desorption of the chloroform and upward diffusion back into the water column are not likely to be high compared to those observed during the initial dissolution period.

Following the chloroform spill, chloroform concentrations were measured at several locations in the Mississippi River below the spill. Figure IV-55a shows the time history of the chloroform concentration at a location 16.3 miles below the spill for the first 60 hours following the spill. A more compressed time scale is shown in Figure IV-55b and illustrates how the concentrations varied for 20 days following the spill. The peak concentration passes very rapidly (on the order of 1 day) and the maximum observed concentration is about 365 ppb. At this location, the chloroform is approximately well-mixed with the river at this point (Neely _et al._, 1976).

Based on Figure IV-55b the total amount of chloroform passing the location can be estimated as follows:

$$\text{Mass} = \int CQdt = Q \int Cdt$$

The right-most integral is simply the area under the concentration-time curve in Figure IV-55b. Without showing the calculations, the total mass of chloroform (above background) which passes the location 16.3 miles below the spill is about 300,000 kg. Since the total amount of chloroform spilled was about 800,000 kg, more than half of the chloroform was unaccounted for. It is unlikely, as earlier calculations showed, that diffusion and sorption

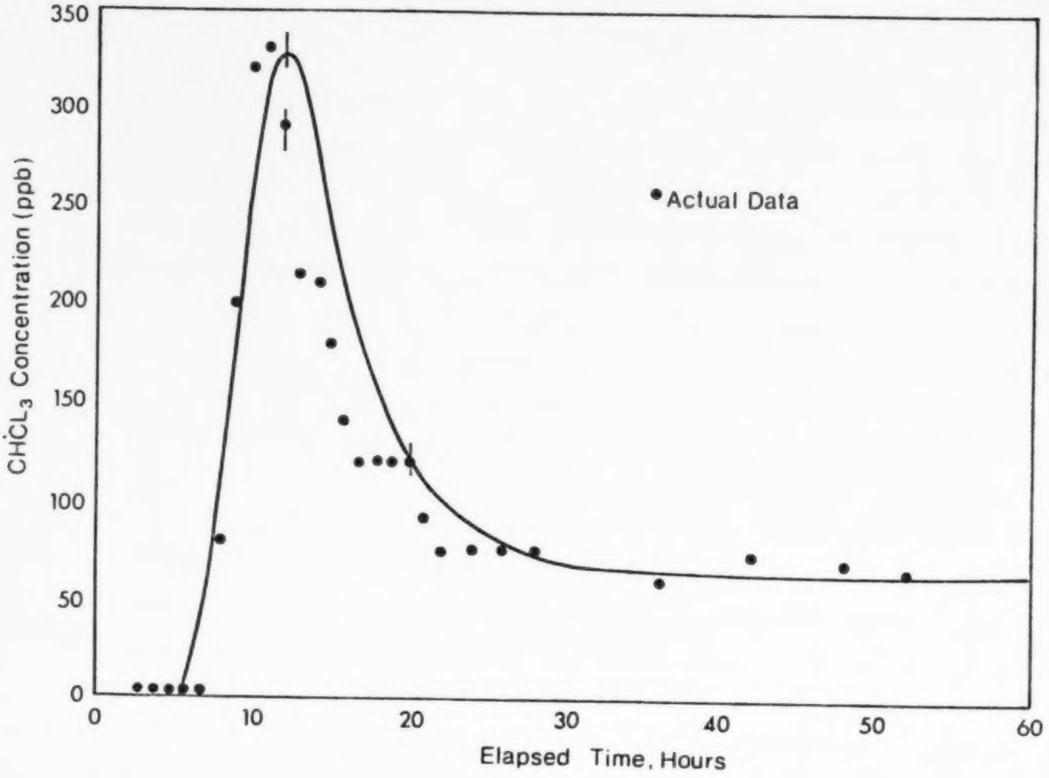


FIGURE IV-55A CHLOROFORM CONCENTRATION IN WATER COLUMN FOR FIRST 60 HOURS FOLLOWING A SPILL 16.3 MILES UPSTREAM.

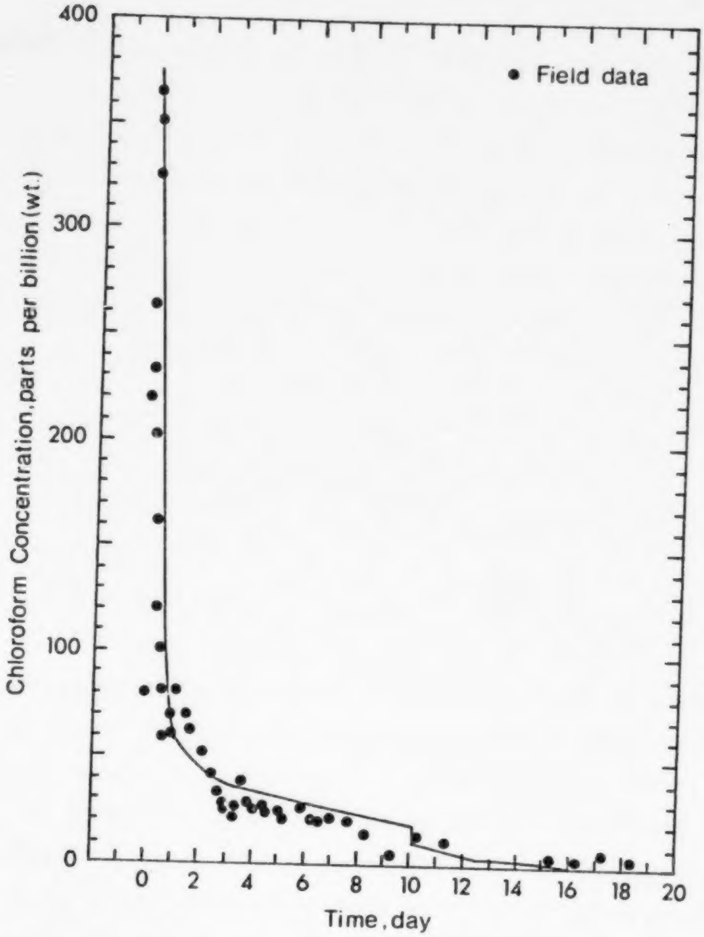


FIGURE IV-55B CHLOROFORM CONCENTRATION IN THE MISSISSIPPI RIVER AT A LOCATION 16.3 MILES BELOW THE AUGUST 19, 1973 SPILL.

into the bottom sediment was significant. Volatilization could be important and will be discussed shortly.

The observed results shown in Figure IV-55a are compared against those predicted in this example. A concentration of 850 ppb was predicted just below the spill site; the maximum shown in Figure IV-55a is 365 ppb. It is expected, for several reasons, that the concentrations 16.3 miles below the spill site will be less than at the spill site. First it is probable that additional dilution occurred as the chloroform was transported to the sampling site. An estimate of the dilution can be attained by multiplying the river width by the spill width, or:

$$\frac{4000}{260} = 15$$

The well-mixed concentration becomes:

$$\frac{850}{15} = 60 \text{ ppb}$$

Comparing this to Figure IV-55a, it is noted that this value approximates the average concentration following an elapsed time of about 20 hours, but misses the peak during the first 20 hours. There may be a number of factors responsible for this behavior, and one of the most important will be examined here. During the spill of chloroform, it was estimated that about 10 percent, or 80,000 kg were transported downstream directly without ever reaching the river bottom. The travel time to the sampling site is:

$$\frac{16.3 \text{ mi}}{1.26 \text{ mph}} = 13 \text{ hours}$$

Figure IV-55a shows that this coincides with the arrival of the peak at mile 16.3. The peak concentration can be estimated using Equation IV-140 presented earlier. The diffusion coefficient is approximately 210 m^2/sec (McQuivey et al., 1976) for the lower Mississippi River. The predicted peak in concentration at mile 16.3 is:

$$C = \frac{80000 \times 10^3}{2 \times 4000 \times 36.3 \times (.3048)^2 \sqrt{\pi \cdot 210 \cdot 3600 \cdot 13}} = 520 \text{ ppb}$$

This concentration is somewhat higher than the maximum 365 ppb observed, but this is to be expected since Equation IV-140 assumes the mass is input instantaneously, while in reality about 8 hours elapsed. Further if the concentration due to the dissolved portion of the spill is calculated at 20 hours, a concentration of 15 ppb is obtained. This illustrates that the mass due to initial dissolution has almost passed the sampling location, and the remaining contribution to the elevated concentrations measured is due largely to dissolution of chloroform which has settled on the river bottom. It appears that there are two basic phenomena which account for the measured concentration-time profile: an initial period of dissolution of chloroform (less than 1 day) before it settles to the bottom, and a subsequent period (10 to 15 days) of dissolution of settled chloroform.

The absence of an adequate mass balance between the amount of chloroform which entered the river as a result of the spill and the amount which passed a location 16.3 mi below the spill has not been addressed. Volatilzation losses could be one reason for the imbalance.

Equation IV-123 can be used to estimate the volatilization losses. Since the chloroform was initially deposited on the bottom of the river, during a portion of the travel distance it was not in contact with the atmosphere, and so volatilization could not occur. The approximate travel time for vertical mixing to occur is (Fischer et al., 1979):

$$t = \frac{0.4\ H^2}{\varepsilon_z}$$

where

H = water depth
ε_z = vertical diffusivity

Choosing an ε_z value of 50 cm^2/sec, based on Fischer et al. (1979) and a depth of 11 m, the travel time required to effect vertical mixing is

$$t = \frac{0.4\ (1100)^2}{50\cdot 3600}\ \text{hr} = 2.7\ \text{hrs}$$

Based on a velocity of 1.85 ft/sec, the travel distance is about 3.3 miles. Hence the pollutant is in contact with the atmosphere for about 13 miles.

Since only the dissolved phase of chloroform volatilizes, the fraction of the total chloroform as solute will be estimated using Equation IV-109:

$$C = \frac{C_t}{1+k_p,S}$$

The partition coefficient K_p was estimated as 1.0. The sediment concentration is about 400 ppm. Hence:

$$\frac{C}{C_t} = \frac{1}{1 + 1 \times 400 + 10^{-6}} \approx 1.0$$

Thus, essentially all the chloroform is dissolved and is available for volatilization.

Henry's Law constant for chloroform can be found based on the data in Table II-5:

- vapor pressure = 150 Torr
- solubility in water = 8200 ppm
- molecular weight = 118.

Henry's Law constant is:

$$\frac{150 \times 118}{760 \times 8200} = 3 \times 10^{-3} \frac{\text{atm}\cdot\text{m}^3}{\text{mole}}$$

From Table II-15 a typical volatilization rate is about 17 cm/hr.

The average chloroform concentrations for the 13 miles above the data collection point are:

200 ppb for 1 day
40 ppb for the next 9 days
10 ppb for the next 9 days

The total amount of chloroform volatilized is (using Equation IV-109):

$$\Sigma\ k_v\ C_i\ A_c\ \Delta t$$

$$= 0.17 \times 24 \times 1200 \times 21 \times 10^3(200 + 40 \times 9 + 10 \times 9 - 5 \times 19) \times 10^3$$

$$= 5.8 \times 10^7 \text{ g} = 58000 \text{ kg}$$

Hence, all of the unaccounted for chloroform (about 480,000 kg) could not have volatilized within 13 miles.

Over 50 percent of the chloroform still remains unaccounted for. It is possible that other transformation processes were operative. The enviromental fate of chloroform in terms of photolysis, hydrolysis, oxidation, and biological degradation was reviewed in Callahan *et al*., 1979. It was concluded that these processes are of minor importance compared to volatilization and so are probably not significant here.

It is possible that the samples of chloroform shown in Figure IV-55b were not cross-sectional averages. The chloroform concentration could have been weighted toward the stream bottom or toward one side. A dye study performed by McQuivey (1976) on the lower Mississippi River showed that 50 miles were required before complete mixing was attained, while the sampling was conducted 16.3 miles below the spill. Even though chloroform does not sorb strongly, there is a possibility that the suspended solids and bed load concentration near the bottom of the river were high enough to cause substantial sorption. Based on the evidence there is a distinct possibility that some of the "missing" chloroform was actually advected past the sampling locations without being detected.

END OF EXAMPLE IV-19

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